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NUMERICAL METHODS FOR THE PREPARATION

OF POTENTIAL ENERGY CURVES OF

DIATOMIC MOLECULES

THESIS

AFIT/GNE/PH/83M-12   Lyle L. Rutger
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NUMERICAL METHODS FOR THE PREPARATION

OF POTENTIAL ENERGY CURVES OF

DIATOMIC MOLECULES

(with applications for lead-oxide)

THESIS

Presented to the Faculty of the School of Engineering

of the Air Force Institute of Technology

Air University

in Partial Fulfillment of the

Requirements for the Degree of

Master of Science

by

Lyle L. Rutger, B.S.

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Graduate Nuclear Engineering

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Approved for public release; distribution unlimited.

Preface

This work has been prepared to provide researchers at the Air Force Institute of Technology and the Weapons Laboratory with the computer programs necessary to analyze spectroscopic data. I am grateful for the learning opportunity provided by this thesis and hope the results are helpful to those who follow me.

I am indebted to my thesis advisor, Dr. Ernest Dorko, for his guidance and encouragement throughout the development of the project. I wish to thank C. R. Vidal for his timely response in providing his program for generating potential energy curves at the start of my research. Finally and foremost, I thank my wife Vivian and children for their support in this endeavor.

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Abstract

This thesis presents the tools necessary to transform spectral data from diatomic molecules into potential energy curves which are most consistent with the experimental data and the quantum mechanical model (i.e., the Schroedinger wave equation (SWE)) for a diatomic molecule. The first of these tools, a computer program called DUNCON, generates spectroscopic constants by performing least-squares fits to spectroscopic data. The program performs fits to separate groups of data and then merges the results in a manner based upon the relative errors and correlations of the separate data sets. The second tool is a computer program provided by C. R. Vidal which contains two major routines. The first routine generates potential energy curves using the Rydberg-Klein-Rees (RKR) method. The second routine through an inverted perturbation analysis (IPA) adjusts the RKR curve so it is consistent with the SWE model. Finally, techniques are presented for extending potential energy curves to the dissociation energy, D_e, when the spectroscopic data alone is inadequate for the purpose.

Use of the programs is demonstrated for the diatomic molecule lead-oxide. Constants are produced for the A, B, D, a, b, and X states from previously published experimental

data. A new set of assignments is made for the b state
experimental data producing constants with significantly
improved accuracy over those reported in literature. The
b state constants are:

$$T_e = 16325.1 \pm 11.2 \text{ cm}^{-1}$$

$$W_e = 430.99 \pm 2.47 \text{ cm}^{-1}$$

$$W_e X_e = -0.757 \pm 0.441 \text{ cm}^{-1}$$

These are one standard error limits. Potential energy curves
are generated for the a, A, and X states of lead-oxide. The
X state potential energy curve is extended to its dissociation
energy.

NUMERICAL METHODS FOR THE PREPARATION

OF POTENTIAL ENERGY CURVES OF

DIATOMIC MOLECULES

I   Introduction

The construction of accurate potential energy curves
is essential to the understanding of data gathered in pur-
suits ranging from the study of gas kinetics to the study of
stellar structures. Potential energy curves are used to
calculate Franck-Condon factors which can be used to predict
the probabilities of an electronic transition. Discussed in
this paper are Dunham coefficients with the corresponding
model used to represent experimental data. A computer program
called DUNCON is developed for generating a minimum-variance
linear unbiased (MVLU) fit to independent sets of spectro-
scopic data. This program has a provision for merging these
fits, as appropriate, to obtain weighted, correlated estimates
of constants for data sets which exhibit different accuracies
or are correlated.   The Rydberg-Klein-Rees (RKR) method of
generating potential energy versus internuclear separation
curves is presented. A computer program which performs RKR
calculations and then uses an inverted perturbation approach
(IPA) (Ref 23) to improve the accuracy of the RKR curve is

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discussed in detail. The RKR-IPA program was developed by C. R. Vidal and H. Scheingraber (Ref 41). Utility of the programs is demonstrated using data reported for the diatomic molecule lead oxide (PbO).

The accuracy of any potential energy curve depends upon the analytic model used to represent experimental data and the manner in which the constants in the model are generated. The Dunham model was chosen to represent the data because of the large number of terms that can be incorporated.

The RKR method is a semi-classical WKB method which has been shown to agree quite well with quantum mechanical calculations for simple molecules (Ref 34). Because of its accuracy, it has been chosen by several researchers to ascertain the accuracy of other methods such as the Morse formula for generating potential curves (Refs 47 and 32).

A recent improvement on the RKR method, though still an approximate method, is the IPA approach which starts with an RKR curve and adjusts it to obtain an approximate but more accurate solution to the Shroedinger equation.

Methods developed by Leroy, by Tellinghuisen, and by Vidal and his coworkers are discussed. These methods can be used to extend potential energy curves when the available experimental data does not cover the entire range of the potential curve.

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II Literature Background and Theory

Modeling Spectroscopic Data for Diatomic Molecules

Spectroscopic data resulting from the emission of energy by a diatomic molecule during a transition from an excited electronic state to a lower state may be represented as follows:

$$\nu \, (v',J',v'',J'') = T'(v',J') - T''(v'',J'') \qquad (1)$$

where ν is the observed line frequency in wave numbers, and the term values for the upper and lower electronic states, T' and T'' respectively, are represented by the Dunham type expression:

$$T(v,J) = \sum_{ij} A_{ij}(v + 1/2)^i \, J^j \, (J + 1)^j \qquad (2)$$

(Ref 48:1866).

Although Eq (2) has the same form as that associated with the Dunham coefficients, Y_{ij} , (Ref 18), i.e.,

$$T(v,J) = \sum_{ij} Y_{ij}(v + 1/2)^i \, J^j \, (J + 1)^j \qquad (3)$$

researchers M. M. Hessel and C. R. Vidal make the distinction that their A_{ij} values are not necessarily identical to Dunham's Y_{ij}'s (Ref 22:4443).

Dunham arrived at the expression in Eq (2) by using the Wentzel-Brillouin-Kramer method (WKB) (Refs 51; 9 and 29) to solve the Schroedinger equation for the rotating diatomic vibrator for the energy levels within one electronic state:

$$\frac{d^2\psi}{d\xi^2} + \frac{8\pi^2\mu r_e^2}{h^2}\left[E - V(\xi) - \frac{h^2}{8\pi^2 r_e^2 \mu}\frac{J(J+1)}{(1+\xi)^2}\right]\psi = 0 \qquad (4)$$

where:

$\xi = (r - r_e)/r_e$

r_e = the equilibrium nuclear separation

μ = the reduced mass

V = potential of the function, with a minimum at r_e

V_r = the last term which is due to the centrifugal force of rotation.

He expressed the potential energy by expanding V about $\xi = 0$.

$$V = hca_0\xi^2(1 + a_1\,\xi + a_2\,\xi^2 + a_3\,\xi^3 + ...) \qquad (5)$$

where $a_0 = w_e^2/4B_e$; w_e is the classical frequency of small oscillations expressed in cm-1 and $B_e = h/(8\pi^2\mu r_e\,c)$ (Ref 18:732). Finally, he obtained expressions for the Y_{ij}'s in terms of the a_k's in Eq (5).

Hessel and Vidal distinguish their constants, A_{ij}, from the Dunham constants, Y_{ij}, by pointing out that the latter are theoretically derived, while the A_{ij}'s are the results of a least-squares fit. Inherent in the least-squares

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fitting procedure is the fact that the A_{ij} coefficients absorb the effects of inaccuracies in the data, and are somewhat dependent upon the values of their neighboring constants and upon any missing constants (Ref 22:4447). For these reasons, the A_{ij}'s are only estimates of the theoretical Y_{ij} derived by Dunham.

Some further discussion of the A_{ij} and Y_{ij} constants is appropriate. First, a listing of the correspondence of Dunham's constants and the classical spectroscopic constants is desirable. They are given in Table I-1.

TABLE I-1

Correspondence Between Dunham Coefficients and
Classical Spectroscopic Constants

Y_{00}^{*}	$Y_{01} \sim B_e$	$Y_{02} \sim D_e$ $Y_{03} \sim F$ $Y_{04} \sim H$
$Y_{10} \sim w_e$	$Y_{11} \sim -\alpha_e$	$Y_{12} \sim \beta_e$
$Y_{20} \sim -w_e x_e$	$Y_{21} \sim \gamma_e$	
$Y_{30} \sim w_e y_e$		
$Y_{40} \sim w_e z_e$		

*Y_{00} is defined as:

$$Y_{00} = 1/4\ Y_{20} + 1/4\ Y_{01}\ ((Y_{11}Y_{10}/(6\ Y_{01}^{2})) - 1)^{2} \qquad (6)$$

This is the expression normally reported in the literature based upon the work of Dunham (Ref 18), although the expression for Y_{00} is not explicity stated in Dunham's work. Sandeman

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(Ref 40) and Jarmain (Ref 25) expand on Dunham's work. Using this material, the expression given in Eq (6) can be verified. In addition to this derivation, the expression for Y_{00} was found in the following works: (Refs 49; 28:325; 35:117; and 41:4450). The expression for Y_{00} was found to be in error in two publications. First, Herzberg's Y_{00} is larger than that in Eq (6) by $+3/4\ Y_{20}$ (Ref 21:109). Second, in McKeever's work, due to a typographical error, "$+1/4\ Y_{20}$" was omitted (Ref 3:47). The works of Sandeman and Jarmain compliment Dunham's work, making easier the understanding of Dunham's work.

Returning to Eq (1), it should be noted that when a least-squares fit is performed using Eq (2), the bottom of the potential energy curve of the lower state is typically assigned a value of "0." This is done by omitting the A_{00}'' term from the fit. When A_{00}' is found from the least-squares fit, it is not equivalent to Dunham's Y_{00}' for the upper state. For this reason, Vidal assigns an asterisk to A_{00}' and calls it A_{00}^{*} . This term is made up of three components as shown (Ref 44):

$$A_{00}^{*} = A_{00}' + Te - A_{00}'' \tag{7}$$

A_{00}' and A_{00}'' are estimated from Eq (6). These A_{00}' and A_{00}'' are then the best estimates of Dunham's Y_{00}' and Y_{00}'' . Eq (7) can be solved for Te' , the electronic term energy of the upper state:

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$$Te = A_{00}^{*} - A_{00}' + A_{00}''$$ (8)

In applying Dunham's expression, one should be aware of its inadequacies. Expressions such as the Morse potential (Ref 21:57):

$$U(r-r_e) = D_e (1 - \exp(-B(r-r_e)))^2$$ (9)

are constructed to guarantee that as $r \rightarrow r_e$, $U \rightarrow 0$ and as $r \rightarrow \infty$, U approaches the dissociation energy, D_e . Eq (5) on the other hand does not necessarily satisfy these two criteria. Sandeman showed that if Morse's equation is expanded about $(r-r_e) = 0$, it takes on a form similar to Dunham's Eq (5), but is expressed in terms of two constants and additional numerical coefficients as follows:

$$U = a_0(1 - a + 0.583a^2\xi - 0.250a^3\xi + 0.086a^4\xi$$
$$- ...) \quad (10)$$

A comparison of Eqs (5) and (10) shows that Dunham's expression is a more general form of Morse's equation. Sandeman also applies a similar expansion to an equation for potential energy developed by Kratzner (Ref 30) and obtained a similar correspondence with Dunham's expression. Because of the increased number of variables and, in turn, the increased flexibility, Dunham's expression has the potential for being more accurate. But, because of this freedom, obtaining constants which satisfy the convergence criterion is more difficult and is not guaranteed for large values of r or v .

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Jarmain made a term-by-term comparison of similar expressions developed from Dunham's work and by the RKR method and showed that, upon neglecting Dunham's small corrections, the potentials produced by the two are mathematically identical (Ref 25:217). Based upon this, the use of Dunham's expression (Eq (3)) to represent spectroscopic data for input to an RKR program for generating potential curves is justified and appropriate.

In applying Dunham's expression, one should remember that his equations are developed for small oscillations about r_e . At energy levels approaching the dissociation limit, Eq (2) may no longer be appropriate. Eqs (1) and (2) are for simple cases. In cases where Λ-type doubling occurs, or where isotopic effects are being considered, more complex models must be substituted for Eqs (1) and (2). Works cited in the bibliography by Vidal and his coworkers present variations of Eq (2).

Spectroscopic Constants by Merging Least-Squares Fit Data

The large quantities of data obtained in a spectroscopic analysis requires that the data be reduced to a more manageable form. For example, Eqs (1) and (2) in the previous section are used to calculate reportable constants. To make these models usable, the A_{ij} coefficients must be determined. The most widely used method of generating these coefficients

is to perform a linear least-squares fit to the experimental data. For spectroscopic data, a model is created, typically involving a power series expansion based upon the rotational and vibrational quantum numbers as expressed in Eqs (1) and (2). If only band head data is being analyzed, the model takes the following form:

$$\nu = \sum_{i\,0} A'_{i0} (v' + 1/2) \; - \; \sum_{i\,0} A''_{i0} (v'' + 1/2)^{i} \qquad (11)$$

If several different transitions are involved, different values of the A''_i ground state constants may be obtained. In addition, the accuracy of the A''_i's may be different. It is desirable to merge these constants and obtain a best estimate of the ground state constants. This can be done by accomplishing a weighted least-squares fit of the data. Such a merging can produce more accurate estimates of the constants and reduce the error limits associated with them. The merged fit may also improve the upper state constants.

Merging may also be desirable for the case when two groups of data are available with significantly different standard errors. For example, if infrared data for vibration-rotation band transitions and microwave data for transitions between adjacent rotational levels are available, the greater accuracy of the microwave data can improve the accuracy of the other constants if a weighted merged fit is performed.

There are other methods of data fitting available. These methods include least absolute deviation, least-squares

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deviation, maximum likelihood, and minimum chi-squared. All have different fit criteria (Ref 2:3). Also, nonlinear least-squares fits are possible (Refs 4 and 15). The present report deals only with the least-squares fit techniques.

The least-squares method or "regression" method minimizes the sum of the squared deviations between observed values and values calculated using the constants obtained from the fit. The least-squares method provides the minimum-variance linear unbiased (MVLU) estimates of the constants; that is, the least-squares method introduces no bias. The fits produced are linear functions of the data. When the fit is used to reproduce data, the generated data exhibits the smallest possible variance from the original data that can be achieved with the model and data used (Ref 2).

In performing a least-squares fit, the following assumptions are made:

1. The model (equation) chosen to represent the data is a perfect description of the physical event.

2. The model is linear in the constants to be estimated.

3. The mean error of the experimental data is zero. Any systematic error present must be small compared to the variances and random errors of the data.

4. The variance-covariance elements must be finite and their relative values known if different groups of data are to be merged (Ref 2:7).

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In reducing spectroscopic data, three methods are
available:

1. The reduction of each band, i.e., each a group of
transitions from one electronic state to another, separately.

2. The reduction of a number of bands simultaneously.

3. The reduction of the bands separately and then
merging the resulting data.

The first and third techniques are developed in this
paper. The method of approach is now described. Least-squares
fitting techniques are based upon the following matrix equation:

$$\nu = X\beta + \varepsilon \qquad (12)$$

where ν is a column matrix containing the experimentally
observed line frequencies expressed in wavenumbers, X is
a matrix made up of the $(v + 1/2)$ and the $J(J + 1)$ terms
as dictated by the model in Eqs (1), (2), or (11) as chosen.
β is a column matrix made up of the A_{ij} constants which are
to be calculated. The ε column matrix contains the unknown
errors associated with each observed experimental data point.
These matrices are written out explicity in Appendix A to
aid the user in understanding the program DUNCON.

Eq (12) is then solved for β as:

$$\beta = (X^T X)^{-1} X^T \nu \qquad (13)$$

The estimated variance of the fit is expressed as follows:

$$\sigma^2 = (\nu - X\beta)^T \; (\nu - X\beta)/f_m \qquad (14)$$

where f_m is the degree of freedom of the calculation. The degrees of freedom, f_m, is equal to the number of experimental values ν used in the fit minus the number of constants to be obtained in the β matrix. The variance-covariance matrix for the constants obtained in Eq (13) is calculated by the following relation:

$$\theta = \sigma^2 \; (X^T X)^{-1} \qquad (15)$$

The diagonal elements of the θ matrix are the variances of the constants and the off diagonal elements are their covariances. The correlation between the calculated constants is expressed by the correlation coefficients which are obtained using the variances and covariances in the following manner:

$$C_{ij} = \theta_{ij}/(\theta_{ii}\theta_{jj})^2 \qquad (16)$$

The subscripts refer to the two constants for which the coefficient expresses the correlation.

As mentioned earlier, the performance of separate fits to each band will yield several values for the constants associated with the lower electronic state. The variances for different bands may also differ significantly. If the variances of the bands are the same, the data can be combined

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in one large data group and reduced simultaneously. If
estimates of the errors are available, a weighted fit based
upon the error may and should be performed.

Albritton describes an approach, the correlated
least-squares fit, which is more general than the weighted
least-square fit (Refs 2 and 3). Albritton showed that one
need not use all raw data at one time to obtain a merged fit.
He showed that a weighted simultaneous multiband fit and a
merged band-by-band fit are equivalent. The merged fit is
presented in this paper.

The bands or other groups of data are first reduced
in a least-squares manner as previously discussed.

Then the data obtained in the initial least-squares
fit may be expressed in the following manner:

$$y = X\beta^M + S \tag{17}$$

where y is a column matrix made up of the constants obtained
from the separate least-squares fits and β^M is a column
matrix which will hold the desired merged constants. The
y matrix will often contain several values for the same
constant. Each constant will be represented only one time in
the β^M matrix. The X matrix relates the redundant values
in the y matrix to the corresponding constants in the β^M
matrix. Explicit examples of these matrices are given in
Appendix A.

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To perform a weighted, correlated least-squares fit, a matrix composed of the variance-covariance matrices from a separate least-squares fit is required. This matrix is given the symbol "θI." It is structured as follows:

$$\theta I = \begin{bmatrix} \theta_1 & 0 & 0 \\ 0 & \theta_2 & 0 \\ 0 & 0 & \theta_3 \end{bmatrix} \qquad (18)$$

where θ_1, θ_2 and θ_3 are the variance-covariance matrices of Eq (15). The formula required to obtain the merged constants is as follows:

$$\beta^M = (X^T \theta I^{-1} X)^{-1} X^T \theta I^{-1} y \qquad (19)$$

The estimated variance of the new merged fit is given by:

$$\sigma^2 = (y - X\beta^M)^T \theta I^{-1} (y - X\beta^M)/f_m \qquad (20)$$

where f_m is the degree of freedom. The variance-covariance matrix of the merged constants is obtained by the following calculation:

$$\theta^M = \sigma^2 (X^T \theta I^{-1} X)^{-1} \qquad (21)$$

The formulas are discussed in future detail in the appendices.

As in all analysis, the data should be checked to insure that the errors predicted by the least-squares fit follow a normal distribution pattern. Albritton provides a

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fairly complete discussion of the checks commonly used
(Ref 2:14-31).

Having established that the errors of the data are
normally distributed, one should then construct confidence
limits for the constants based upon the degrees of freedom
and the confidence one wishes to have that the true value
is within the assigned limits. The placing of too much
reliance upon error limits specified by one standard devia-
tion, $1 \times \theta_{ii}^{\frac{1}{2}}$, should be avoided. Even if a large sample of
data is taken, one can only be about 68% certain that the
"true value" lies within a range of $\pm 1 \times \theta_{ii}^{\frac{1}{2}}$. If a 95%
confidence level is desired and the degrees of freedom, f_m ,
is greater than 30, one must assign limits of $\pm 2 \times \theta_{ii}^{\frac{1}{2}}$.
The multiplier of $\theta_{ii}^{\frac{1}{2}}$ is student's t-factor. It is named
after its originator, W. S. Gosset (1876-1937). It is a func-
tion of the degrees of freedom of the calculation and the
desired confidence level, "$1-\lambda$." Dixon and Massey (Ref 17)
give a tabulation of student's t-factor as a function of the
degrees of freedom and the degree of confidence. The confi-
dence limits for the constant are then expressed as follows:

$$\beta_i + t(f_m, \ 1-\alpha) \theta_{ii}^{\frac{1}{2}} \tag{22}$$

Having established the limits, one can assume that the proba-
bility of the true value of falling within the limit
$\pm t \theta_{ii}^{\frac{1}{2}}$ is "$1-\alpha$" where α may vary between 0 and 1.

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With the confidence limits for the estimated constants properly established, one can then determine if the constants are significant (Ref 27). For example, if a constant has a value of 3 and an assigned error limit of ±5, the range in which the true value of the constant might be found is -2 to +8. This range includes 0; hence, the constant is not significant. If the assigned confidence limits, $\beta_i \pm t\theta_\alpha^{\frac{1}{2}}$ includes zero, then the constant is insignificant and may normally be discarded. Two exceptions to this rule may be encountered.

The first exception concerns the case where a non-zero correlation between two molecular constants exists. If non-zero correlation coefficients are involved, standard errors must be calculated using the most general formulation involving both variances and covariances. If large correlations exist, the rounding of a constant to the number of significant digits dictated by the standard error of the constant, may result in loss of information, i.e., rounding may introduce unnecessary inaccuracies into the calculated data (Ref 2:2).

Albritton suggests that one digit beyond the "one standard error digit" should suffice for most fits. A simple check is to use the rounded constants and see that they reproduce to some desired accuracy the values calculated using the unrounded constants obtained from the fit.

The second exception occurs, where it may prove necessary to retain a constant when not justified by the standard

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error, in the extension of the potential curve to its dissocia-tion limits (Ref 10:83).

Before merging data from separate least-squares fits, a check should be made for systematic errors. A simple check is to verify that for a given set of confidence limits, say 95%, the error limits for the common constants obtained in two independent fits overlap each other. If they do not, then it is probable that one set contains a systematic error. A second more sophisticated test involves the computation of the confidence limits for the differences for pairs of corresponding constants checking to see if they include zero (Ref 2:45). Calculation of the confidence limits of differences involves student's t-factor and methods are given by Bennet and Franklin (Ref 5); and Dixon and Massey (Ref 17). A more extensive discussion of the covariance-variance data and how it may be used is presented by Albritton (Refs 2 and 3).

Finally, Albritton provides a recommendation as to what data should be provided in a report on the results of a spectroscopic study. He lists the following as essential data:

1. The observed line numbers (with assignments).

2. If room permits, the variance-covariance matrix used to merge the data.

3. The model used to represent the experimental data.

4. The estimated molecular constants.

5. The standard error of the constants and the degrees of freedom involved in the calculations. This data will enable the reader to establish his own confidence limits.

6. The estimated variance of the variance, σ_σ, may be helpful. An estimate of this value for large samples of normally distributed data may be obtained by the formula (Ref 16):

$$\sigma_\sigma = \sigma/[2f_m]^{\frac{1}{2}} \tag{23}$$

Other data which may be appropriate include the variance-covariance matrix of the final merged constants and the results of the testing to determine the normality of the data sample.

Rydberg-Klein-Rees Potential Energy Curves

Potential energy curves for diatomic molecules are plots of potential energy versus the internuclear distance between atoms. Figure II-1 shows a typical curve. From this plot of energy versus internuclear distance, it can be seen that as the nuclei approach each other the potential becomes infinite; and as their separation increases, the curve asymptotically approaches the dissociation energy, D_e. The equilibrium internuclear distance, r_e, is the distance at which the potential energy of the molecule is at a minimum.

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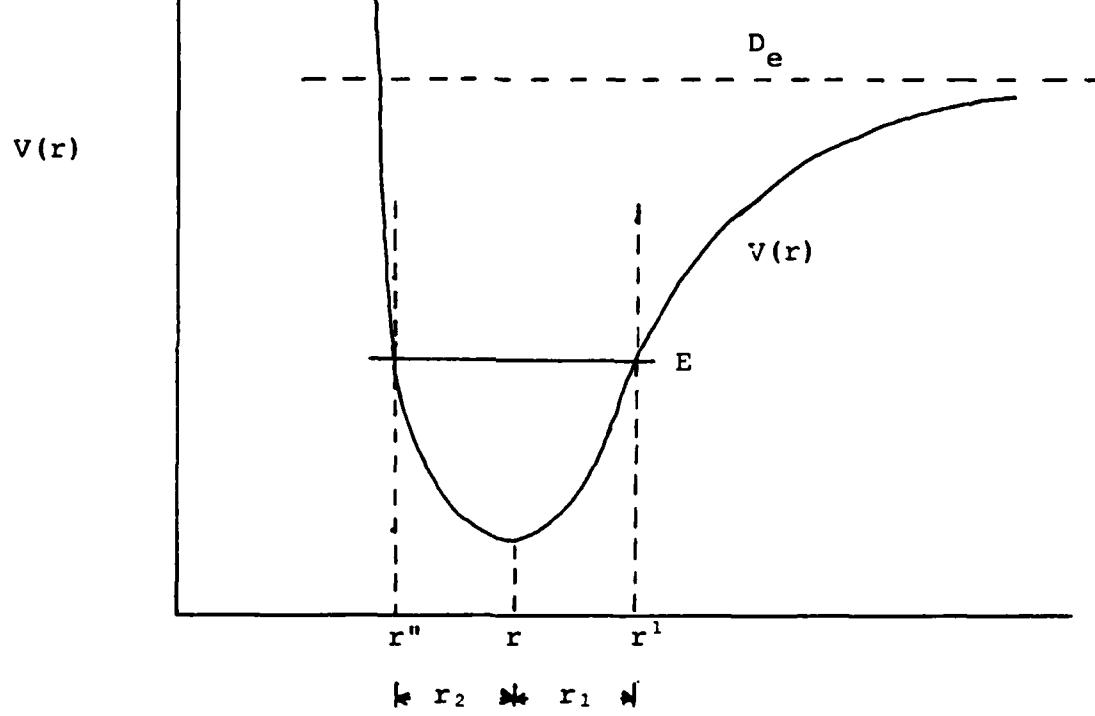
Fig II-1. Potential Energy Versus Internuclear Distance
for a Diatomic Molecule

The Rydberg-Klein-Rees (RKR) model for the potential energy curve is developed in this section. Rydberg started with the expression for the total energy, E , for a rotating-vibrating diatomic molecule:

$$E = p^2/2\mu + V(r) \tag{24}$$

The $p^2/2\mu$ term in Eq (24) is the kinetic energy of the system, p in turn, is the linear momentum. The second term, V(r) is defined as follows:

$$V(r) = U(r) + \kappa/r^2 = U(r) + P^2/2\mu r^2 \tag{25}$$

where U(r) is the potential energy of the system, P is the angular momentum of the system, and μ is the reduced mass.

Based on this energy expression, Rydberg developed a procedure for graphically determining the classical turning points for a diatomic molecule (Ref 39). Klein modified Rydberg's derivation so that the turning point could be calculated numerically (Ref 52). Reese obtained quadratic and cubic analytic solutions approximating Klein's formulas (Ref 38).

Klein's mathematical development is given here. Terms used in the development are shown in Fig II-1 as an aid in following the presentation. The classical turning points are deisnged $r´$ and r''. Klein defined the turning points in terms of the quantities r_1 and r_2 . For his analysis,

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r_1 and r_2 are measured from r_e , r_1 being positive
and r_2 negative. Then r' and r'' are defined as follows:

$$r' = r_1 + r_e \tag{26}$$

$$r'' = r_e + r_2 \tag{27}$$

Then

$$dr' = dr_1 \tag{28}$$

$$dr'' = dr_2 \tag{29}$$

$$dr = dr_1 \text{ or } dr_2 \tag{30}$$

Klein designated the width of the potential curve as $2f$ and
from Eqs (26) and (27), it follows that:

$$2f = (r_1 + r_e) - (r_2 + r_e) = r_1 - r_2 \tag{31}$$

The energy in Eq (24) may be expressed as a function of
"I," the action integral for a rotating vibrator and "κ."
These terms are defined as follows:

$$I = \oint P dr \tag{32}$$

$$\kappa = P^2 / (2\mu) \tag{33}$$

The following relationships which involve the period,
τ , and the average position of a harmonic oscillator, $\overline{1/r}$,
are known:

$$1/\tau = \partial E / \partial I \tag{34}$$

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$$\overline{1/r^2} = (\partial E/\partial \kappa) \qquad (35)$$

$$\rho = \tau(\partial E/\partial \kappa) \qquad (35')$$

Using Eqs (32) and (34) and solving for the differential of
E and adding the results, the following is obtained:

$$\delta E = (1/\tau)\delta I + (\rho/\tau)\delta \kappa \qquad (36)$$

Inverting Eq (32), the following is obtained:

$$\tau = \partial E/\partial I \qquad (37)$$

Setting Eq (36) equal to zero and solving for ρ , the follow-
ing is obtained:

$$\rho = -\partial I/\partial \kappa \qquad (38)$$

From the equation for the momentum, $p = \mu v = \mu(dr/dt)$, one
can, by integrating over one cycle, obtain an expression for
the period of vibration for a harmonic oscillator:

$$\tau = \oint \mu(dr/p) \qquad (39)$$

Solving Eq (24) for p and substituting into Eq (39), the
period of oscillation may be expressed as:

$$\tau = (\mu/2) \oint (E-V(r))^{-\frac{1}{2}}dr \qquad (40)$$

The integral in Eq (40) can be broken into two parts,
one to be integrated from r_e to r_1 , and the other from
r_2 to r_e (as depicted in Fig II-1). This operation yields:

$$\tau = 2(\mu)^{\frac{1}{2}} \left[\int_{r_e}^{r_1} dr/(E-V(r))^{\frac{1}{2}} - \int_{r_2}^{r_e} dr/(E-V(r))^{\frac{1}{2}} \right] \quad (41)$$

The factor of two is introduced to account for one vibration cycle from r_e through r_1 and r_2 and back to r_e again. Rearranging Eq (41) and recombining the integrals, one obtains:

$$\tau = (2\mu)^{\frac{1}{2}} \int_{r_2}^{r_1} (dr_1-dr_2)/(E-V(r))^{\frac{1}{2}} \quad (42)$$

Now to change the variables of integration, Klein defined the following terms:

$$y = V(r) - V(r_e) \quad (43)$$

and

$$x = E - V(r_e) \quad (44)$$

where x is constant for a given E . Then r may be expressed as a function of y as follows:

$$r = r_1(y), \quad r > r_e \quad (45)$$

$$r = r_2(y), \quad r < r_e \quad (46)$$

and when at r_e , $r_1(0) = r_2(0) = r_e$. Subtracting Eq (43) from Eq (44):

$$x - y = E - V(r) \quad (47)$$

and if the "f" of Eq (31) is function of y , then as defined

$$r_1(y) - r_2(y) = 2f(y) \qquad (48)$$

then

$$dr_1/dy - dr_2/dy = 2df(y)dy \qquad (49)$$

or

$$dr_1 - dr_2 = 2f'(y)dy \qquad (50)$$

Using Eqs (45), (46), (47), and (50) to change the variable of integration and integration limits in Eq (42), Klein obtained:

$$\tau = 2 (2\mu)^{\frac{1}{2}} \int_{y_2}^{y_1} 2 f'(y) \, dy/(x-y)^{\frac{1}{2}} \qquad (51)$$

From Eq (43) when $r = r_e$, then $V(r) = V(r_e)$ and $y = 0$. Thus, the integral in Eq (51) may be evaluated from 0 (defined as the bottom of the potential well) to some value X .

$$\tau = 2 (2\mu)^{\frac{1}{2}} \int_{0}^{x} f'(y) \, dy/(x-y)^{\frac{1}{2}} \qquad (52)$$

This is the first of two integral equations central to Klein's derivation.

Combining Eqs (28), (35), (35'), and (40) yields:

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$$\rho = \tau \overline{(1/r^2)} = (\mu/2)^{\frac{1}{2}} \oint (1/r^2) \, [dr/E-V(r))^{\frac{1}{2}}] \qquad (53)$$

By definition:

$$dr/r^2 = -(1/r) \qquad (54)$$

Then Eq (53) becomes:

$$\rho = -(\mu/2) \oint d(1/r)/(x-y)^{\frac{1}{2}} \qquad (55)$$

Again, the integral in Eq (55) may be broken into two parts. Then for $r > r_e$:

$$r'' = r_2 + r_e \qquad (56)$$

$$1/r'' = 1/(r_2 + r_e) \qquad (57)$$

and if r_e is set equal to "0" then:

$$1/r'' = 1/r_2 \qquad (58)$$

Similarily for $r < 0$:

$$1/r' = 1/r_1 \qquad (59)$$

Then for small oscillations about r_e , Eq (53) may be written as the difference between the integrals:

$$\rho = 2 \, (\mu/2)^{\frac{1}{2}} \, [\int_{1/r_e}^{1/r_1} -d(1/r_1)/(x-y)^{\frac{1}{2}} - \int_{1/r_2}^{1/r_e}$$

$$-d(1/r)/(x-y)^{\frac{1}{2}}] \quad (60)$$

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$$\rho = (2\mu) \int_{1/r_2}^{1/r_1} d(1/r_2 - 1/r_1)/(x-y)^{\frac{1}{2}} \qquad (61)$$

Klein established the following definition:

$$2g(y) = 1/r_2 - 1/r_1 \qquad (62)$$

Differentiating with respect to y yields:

$$2dg(y) = (d/dy)(1/r_2) - (d/dy)(1/r_1) \qquad (63)$$

Changing the notation yields:

$$2g'dy = d(1/r_2) - d(1/r_1) \qquad (64)$$

Substituting Eq (64) into Eq (61) yields:

$$\rho = 2 (2\mu)^{\frac{1}{2}} \int_0^Y [g'(y)dy/(x-y)^{\frac{1}{2}}] \qquad (65)$$

with the limits of integration assigned in the same manner as for Eq (52). This is the second integral which is central to Klein's derivation.

In the next step of his development, Klein derives expression for r_{max} and r_{min}, the classical turning points for a harmonic oscillator. Klein recognized that the integrals for τ and ρ (Eqs (52) and (65)) were of the Abelian type. He multiplied both sides by $dx/(\alpha-x)^{\frac{1}{2}}$ and integrated both sides from $x = 0$ to $x = \alpha$, where $\alpha = E - (V(r)$ (Ref 35:25), i.e.,

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$$\tau \ dx/(\alpha-x)^{\frac{1}{2}} = 2 \ (2\mu)^{\frac{1}{2}} \int_{y=0}^{y=\alpha} f'dy \int_{x=y}^{x=\alpha} dx/[(\alpha-x)(x-y)]^{\frac{1}{2}} \quad (66)$$

In Eq (66)

$$f'(y) = f(\alpha) \quad (67)$$

and

$$\int_{y}^{\alpha} dx/[(\alpha-x)(x-y)] = dx/(-x^2+y+\alpha-\alpha y)^{\frac{1}{2}} \quad (68)$$

Eq (68) may be integrated as follows (Ref 6:300):

$$\int dx/(uv)^{\frac{1}{2}} = 2/(bd)^{\frac{1}{2}} \ tan^{-1} \ [(-bduv)^{\frac{1}{2}}/bv],$$

$$\text{for } bd>0 \quad (69)$$

where $u = a+bx$, and $v = a'+dx$ and for the present integral:

$$a = \alpha \qquad a' = -y$$

$$b = -1 \qquad d = 1$$

$$bd = -1$$

then the integral can be evaluated to be π . Finally, the left side of Eq (68) is evaluated as:

$$\int_{0}^{\alpha} dx/(\alpha-x)^{\frac{1}{2}} = 2 \ (2\mu)^{\frac{1}{2}}_{\pi} \ f(\alpha) \quad (71)$$

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or solving Eq (71) for $f(\alpha)$:

$$f(\alpha) = 1/(2\pi(2\mu)^{\frac{1}{2}}) \int_0^{\alpha} dx/(\alpha-x)^{\frac{1}{2}} \tag{72}$$

and for $\alpha = y$:

$$f(y) = 1/(2\pi(2\mu)^{\frac{1}{2}}) \int_0^{y} dx/(y-x)^{\frac{1}{2}} \tag{73}$$

Similarily, Eq (65) for "g" may be transformed into the following:

$$g(y) = \frac{1}{2\pi(2\mu)^{\frac{1}{2}}} \int_0^{y} \frac{\rho dx}{(y-x)^{\frac{1}{2}}} \tag{74}$$

From the definitions for x given in Eq (43):

$$dx = dE \tag{74'}$$

Substituting Eq (74') into Eq (34) yields:

$$\tau\, dx = dI \tag{75}$$

Recalling that E is a function of I and κ , and using Eq (47), Eq (73) becomes:

$$f(V) = 1/(2\pi(2\mu)) \int_0^{I} dI/(V-E(I,\kappa))^{\frac{1}{2}} \tag{76}$$

From Eqs (34), (35'), and (74'):

$$\rho\, dx = \rho\, dE = (\partial E/\partial\kappa)\, dE = \tau(\partial E/\partial\kappa)\, (\partial I/\tau)$$

$$= (\partial E/\partial\kappa)\partial I \tag{77}$$

and Eq (74) becomes:

$$g(V) = 1/(2\pi(2\mu)^{\frac{1}{2}}) \int_0^{I'} \partial[E(I,\kappa)/\partial\kappa) \, dI]/(V-E(I,\kappa))^{\frac{1}{2}} \qquad (78)$$

As $E(I,\kappa)$ approaches V in Eqs (76) and (78), the integrals become infinite. To avoid these singularities, Klein instead evaluated the following expression:

$$S(V,\kappa) = 1/(\pi(2\mu)^{\frac{1}{2}}) (V-E(I,\kappa))^{\frac{1}{2}} dI \qquad (79)$$

This expression has the following relation to the f and g of Eqs (76) and (78):

$$f = \partial S/\partial V \qquad g = -\partial S/\partial\kappa \qquad (80)$$

As shown in Eq (2), spectroscopic energy levels can be represented as power series of $(v+1/2)$ and $J(J+1)$. It is convenient then to express the integrals for f and g in terms of the quantum numbers v and J .

The expression for the radial action variable in quantum mechanical terms is

$$I = (v+1/2)h \qquad (81)$$

Then

$$d(I) = d(v+1/2)h \qquad (82)$$

The quantum mechanical expression for κ is:

$$\kappa = P^2/2\mu = J(J+1) \, \hbar^2/2\mu \qquad (83)$$

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Then

$$\partial/\partial\kappa = 2\mu/\hbar^2 (\partial/\partial J(J+1))$$

(84)

Finally, the expressions for f and g become:

$$f(V, J(J+1)) = \hbar/(2\mu)^{\frac{1}{2}} \int_0^{v'+\frac{1}{2}} \frac{d(v+\frac{1}{2})}{[V-E(v+\frac{1}{2}, J(J+1))]^{\frac{1}{2}}}$$

(85)

$$g(V, J(J+1)) = (2\mu)^{\frac{1}{2}}/\hbar \int_0^{v'+\frac{1}{2}} \frac{\partial E/\partial(J(J+1)|_{v+\frac{1}{2}} \; d(v+\frac{1}{2})}{[V-E(v+\frac{1}{2}, J(J+1))]^{\frac{1}{2}}}$$

(86)

where the upper limit of integration v' is selected such that $V = E(v'+1/2, J(J+1))$ for the fixed value of $J(J+1)$ used in the integrals (Ref 35:27,28).

If the RKR calculations are evaluated for $J=0$ then Eq (2) reduces to:

$$T = \sum_{i=1} Y_{i0} \; (v+1/2)^i = G(v)$$

(87)

more commonly referred to as G_v.

Eq (85) becomes:

$$f = \int_{v_0}^{v'} (G(v) - G(v')]^{-\frac{1}{2}} \; dv'$$

(88)

(Ref 24:2), where Kaiser (Ref 26:1686) defined the lower limit of integration by the following:

$$G(v_0) = -Y_{00}$$

(89)

where Y_{00} is the Dunham constant previously defined in Eq (6). The variable v_0 in $G(v_0)$ may be expressed in terms of Dunham coefficients as:

$$v_0 = -1/2 - \Delta = -1/2 - (Y_{00}/Y_{10})(1 + Y_{00}Y_{20}/Y_{10}^2 + \ldots) \quad (90)$$

For $J = 0$

$$\partial E/\partial J(J+1) = \sum_{n=0} Y_{ni}(v+1/2)^n = B(v) \quad (91)$$

(Ref 24:2), where $B(v)$ is the spectroscopic term defined as follows:

$$B_v = B_e - \alpha(v+1/2) + \gamma(v+1/2)^2 \ldots \quad (93)$$

(Ref 21:108).

Using these definitions, Eq (86) for g becomes:

$$g(v) = \int_{v_0}^{v} B(v')(G(v)-G(v'))^{\frac{1}{2}} \, dv' \quad (94)$$

(Ref 24:2).

From the definitions in Eqs (22) and (62) for f and g the following expressions for inner and outer turning points may be obtained:

$$r = (f^2 + f/g)^{\frac{1}{2}} + f \quad (95)$$

Solutions of the equations for f and g are discussed in the section on the RKR Program by C. R. Vidal.

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This completes the theoretical background required for the RKR calculations. Second order semiclassical RKR formulations are not presented in this work. Several articles on the RKR method which were not referenced in this work are listed in Appendix C.

Methods for Extending RKR Curves

In many cases, because of the lack of experimental data, the constants necessary to construct an RKR curve may not be obtainable from straightforward least-square fits or their quality may be insufficient to construct accurate curves. Two techniques for improving existing constants which may, in turn, be used to produce improved RKR curves are presented here (Refs 10; 53).

As depicted in Fig II-1, the potential energy curve of a diatomic molecule should have a minimum at some intermediate distance, approach the dissociation limit for large internuclear separations and increase rapidly as the atoms approach each other. Ideally, curves generated using the RKR method should satisfy these criteria.

For many diatomic molecules, only two and, at most, three vibrational constants are available. The available rotational constants are even more limited. Attempts to generate curves based upon these constants using the RKR method can be expected to produce curves which do not meet the dissociation criteria or which do not exhibit an increasing

potential for small internuclear distances. These results occur because the experimental data upon which the constants are based may represent only a fraction of the vibrational levels which exist between the bottom of the potential well and the dissociation limit.

To develop potential energy curves which obey the known constraints, Leroy and Burns have reported on a new technique which shows promising results. While they start with constants obtained from experimentally observed transitions, they then adjust these constants slightly until the new RKR potential energy curve is most consistent with all of the known constraints.

Leroy and Burns used their knowledge of the desired shape to adjust the constants. They worked with the G_v and B_v quantities as expressed in Eqs (87) and (91). Expressed in terms of these two quantities, their criteria for adjusting the molecular constants are:

1. $V(\alpha)$ assymptotically approaches the dissociation energy (De) and the difference between energy levels, $\Delta G_{v+\frac{1}{2}}$, becomes 0 for the same value of v. $\Delta G_{v+\frac{1}{2}}$ is defined as:

$$\Delta G_{v+\frac{1}{2}} = G(v + 1) - G(v) \tag{95}$$

2. The slope of the inner portion of the RKR curve must be negative. Hence:

$$dV(r)/dr < 0 \qquad\qquad (96)$$

3. The slope of the inner portion of the curve must become increasingly steeper; that is, the second derivative with respect to the internuclear separation must be positive:

$$d^2V(r)/dr^2 > 0 \qquad\qquad (97)$$

A study of Eq (88) reveals that as $\Delta G_{v+\frac{1}{2}}$ becomes smaller, the quantity f becomes larger. In turn, Eq (94) shows that f determines the width of the RKR curve. Examination of Eq (94) further reveals that the value g determines the center of the potential curve for a given energy level. In turn, Eq (93) shows that having determined the constants necessary to generate the $G(v)$'s , the other factor affecting the value of g is $B(v)$, a quantity whose value is determined by the rotational constants, Y_{ni} . From Eqs (88), (93), and (94), it follows that the width of the curve, as determined by the RKR method, and the value at which $\Delta G_{v+\frac{1}{2}} = 0$ depends only upon the vibrational constants which make up Gv . On the other hand, having selected suitable constants for Gv , the behavior of g , the rate at which the outer portion of the curve approaches D_e , and the behavior of the slope of the inner portion of the curve depends solely upon the constants which constitute B_v .

Following this logic, Leroy applied the criteria in 1 above first. If the constants obtained from experimental

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data do not satisfy this criteria, the value of the last experimental constant is adjusted or a value is selected for the next constant, Y_{n_0} , in the series given by expression (8) . The contribution from that constant, $Y_{n_0}(v+1/2)^n$, is then subtracted from the $G(v)$ values calculated from the original experimentally based constants. A least-squares fit is then performed on the adjusted experimental data, $\overset{*}{G}v_j$:

$$\overset{*}{G}v_j = \sum_{i=1}^{n-1} Y_{i0}(v_j+1/2)^i - \left[Y_{n_0}\ (v_j+1/2)^n \right] \tag{98}$$

For a given Y_{n_0} the experimental data fixes the values of the other constants. This new set of constants is tested to determine if Gv approaches a maximum value of D_e . Leroy and Burns say that if this value approaches D_e within $< 2 \text{ cm}^{-1}$ then the criteria in 1 is satisfied. If 1 is not satisfied, then a new trial value for Y_{n_0} is chosen and the process repeated until 1 is satisfied.

At this point, a new RKR curve is generated using the new vibrational constants, Y_{i0} , and the experimental rotational constants, Y_{i1} . The curve is then evaluated according to criteria (2) and (3). If the inner portion of the curve diverges, the process followed for adjusting the constants for Gv is repeated for the constants making up Bv . The value for the last experimental constant is adjusted or a value for the next rotational constant in the

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Y_{i1} series is selected. Then the B_v values given by the experimental constants are adjusted as follows:

$$\overset{*}{B}v_j = \sum_{i=0}^{n-1} Y_{i1}(v_j+1/2)^i - \left[Y_{n1} (v_j+1/2)^n \right] \tag{99}$$

Then a least-squares fit is performed to obtain a new set of rotational constants Y_{01} through Y_{n1} . The new constants are then used to produce a new RKR curve. If the curve does not satisfy the criteria in 2 and 3, then the Y_{n1} constant is adjusted and the process repeated until 2 and 3 are satisfied.

In this manner, Leroy and Burns obtained a set of constants consistent with the experimental data and with criteria 1-3.

Tellinghuisen and Henderson describe a technique for constructing RKR based curves when experimental data does not permit the direct calculation of the rotation constants (Ref 20). Their technique is based upon a combination of the Morse and RKR potentials; hence, Morse-RKR curves.

As explained, vibrational constants provide all the information necessary to calculate f , Eq (88) and, thus, the width of the potential curve, $2f$, as defined by Klein for a given vibrational energy level. Having established the width of a potential, the remaining piece of information required to construct a potential curve is the location of either the inner or outer branches of the potential curve, or

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the center of the potential well, i.e., g as obtained from the RKR calculations.

Tellinghuisen and Henderson point out that inner turning points on a potential curve might be approximated by the Morse potential (Ref 21:101).

$$U(r) = D_e \ (1 - e^{-\beta(r-r_e)})^2 \qquad (100)$$

where:

D_e = dissociation energy, cm^{-1}

r_e = equilibrium internuclear distance, A

$$\beta = 0.12777 \ w_e (\mu/D_e)^{\frac{1}{2}} \qquad (101)$$

where

w_e = the vibration frequency, cm^{-1}

μ = reduced mass, amu

Or because of the relation

$$D = w_e^2/4(w_e x_e) \qquad (102)$$

β may be expressed as follows:

$$\beta = 0.243555 \ (\mu w_e x_e)^{\frac{1}{2}} \qquad (103)$$

Using these relations, Tellinghuisen investigated 25 different well-known potentials and found errors at the dissociation limit for the inner portion of the curve to be typically less than 0.02 $\overset{o}{A}$ and r_e to be in error by seldom more than 1%.

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Further, Tellinghuisen states that a potential curve in error by Δr_{min} has identical classical and almost identical quantum eigenvalues for $J = 0$. The wavefunctions derived from a shifted curve would be skewed with respect to a proper wavefunction.

If possible, Tellinghuisen recommends the construction of curves by formulas (102) and (103) using the experimental w_e and $w_e x_e$. If only w_e and D_e are known, then a value of D_e 40% larger than the experimental D_e should be used.

Tellinghuisen also speculates that α_e might be calculated using an expression derived by Pekeris from the Morse function:

$$\alpha_e = \frac{6\beta_e}{w_e}\left[\left(\frac{w_e x_e}{e}\right)^{\frac{1}{2}} - 1\right] \tag{104}$$

(Ref 21:109). Tellinghuisen found that for 23 of the 25 cases he investigated, the α_e calculated per formula (104) had an average absolute error of 13% and an average signed error of 6%.

If one is seeking the rotational constant D_e (Y_{02}), the following relation might be used:

$$D_e = \frac{4B_e^2}{w_e^2} \tag{104'}$$

(Ref 21:10).

Tellinghuisen cautions against using Bv values made
up of only two terms, i.e.,

$$Bv = B_e - \alpha\ (v+1/2) \tag{105}$$

because the Morse expression for Bv does not terminate with
two terms as does Gv . Further, for high values of v ,
the Morse Bv will differ from the Morse-RKR Bv. The Morse-
RKR Bv value must be determined by numerical methods.

Inverted Perturbation Analysis

Having constructed a semiclassical RKR curve, the
next step is to determine if that curve is consistent with the
Schroedinger wave equation; or, even better, to adjust the
curve so it agrees with the SWE. This leads to the use of the
inverted perturbation approach. The goal of the inverted
perturbation approach (IPA) is to adjust the potential energy
curve of rotationless molecules, $V_0(r)$, so that the
quantum mechanical eigenvalues, E_{vJ} , obtained from a solu-
tion of the Schroendinger wave equation agree in a least-
squares sense with the measured term values, $T(v,J)$.

The IPA technique was first demonstrated by Kosman
and Hinze (Ref 23). Vidal and Scheingraber expanded the use
of the IPA method. Vidal, *in conjunction* with several
authors, has applied the IPA method to a number of molecules.

The Schroedinger wave equation (SWE) for a vibrating
rotator (Eq (4)) is the basis of the IPA method. To develop

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the IPA method, the SWE can be expressed as follows (Ref 41):

$$(H_0^0 + H_{rot}) \; \psi_{vJ}^0(r) = E_{vJ}^0 \psi_{vJ}^0(r) \tag{106}$$

E_{vJ}^0 is the energy eigenvalue specified by the vibration and rotation quantum numbers. H_0 is the Hamiltonian of the non-rotating molecules and is made up of the terms:

$$H_0 = -\left(\frac{\hbar}{4\pi\mu c}\right)\frac{d}{dr^2} + V_0(r) \tag{107}$$

where $V_0(r)$ is the potential energy of the rotationless molecule.

This formulation has been simplified by neglecting terms describing electronic coupling contributions (Ref 46).

The rotational motion of the molecule is described by:

$$H_{rot} = \left(\frac{\hbar}{4\pi\mu c}\right)\frac{J(J+1)}{r^2} \tag{108}$$

In the inverted perturbation approach, one starts with an approximate potential $V_0(r)$, for example an RKR potential. Eq (106) is solved numerically for the zeroth order eigenvalues E_{vJ}^0 and the radial wavefunction $\psi_{vJ}^0(r)$. Then an energy correction ΔE_{vJ} is calculated according to the following formula:

$$\Delta E_{vJ} = E_{vJ} - E_{vJ}^0 \tag{109}$$

where E_{vJ} is the measured term value as calculated from the spectroscopic constants and quantum numbers v and J . If the difference between the experimentally determined term values and the eigenvalues obtained from the SWE is sufficiently small, the calculation is stopped.

If the difference exceeds a specified limit, then one proceeds. As stated, the goal is to obtain some correction to $V_0^0(r)$, i.e., $\Delta V(r)$, such that the calculated and experimental E_{vJ}'s agree. Following this reasoning, then the true potential, $V_0(r)$, being sought may be expressed as a sum of the approximate potential and some delta potential:

$$V_0(r) = V_0^0(r) + \Delta V_0(r) \tag{110}$$

In turn, it follows that the true Hamiltonian differs from the approximate zero order Hamiltonian "$H_0^0 + H''_{rot}$ by $\Delta V_0(r)$:

$$H_0 + H_{rot} = H_0^0 + H_{rot} + \Delta V_0(r) \tag{111}$$

First order perturbation theory gives the following relationship between the perturbation to the Hamilitonian $\Delta V_0(r)$ and and the energy change ΔE_{vJ} :

$$\Delta E_{vJ} = \left\langle \psi_{vJ}^0 \middle| \Delta V_0(r) \middle| \psi_{vJ}^0 \right\rangle \tag{112}$$

To obtain a correction to $V(r)$, a mathematical expression of the following form is assumed to represent $\Delta V_0(r)$:

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$$\Delta V_0(r) = \sum_i c_i f_i(r) \tag{113}$$

The selection of the specific form of the function $f_i(r)$ is critical to the convergence and solution of the SWE. Discussion of the form of $f_i(r)$ will be postponed until the section describing Vidal's IPA program.

Using the $f_i(r)$ and the radial wavefunctions, ψ_{vJ} , obtained from the numerical solution of Eq (106), the expectation values for $f(r)$ are calculated:

$$\left\langle \psi_{vJ}^0 \left| f_i(r) \right| \psi_{vJ}^0 \right\rangle \quad \begin{array}{l} v = 0,1,2,3\dots \\ \\ J = 0,1,2,3\dots \end{array} \tag{114}$$

From Eqs (112) and (113), it follows that:

$$\Delta E_{vJ} = \sum_i c_1 \left\langle \psi_{vJ}^0 \left| f_i(r) \right| \psi_{vJ}^0 \right\rangle \tag{115}$$

Having obtained ΔE_{vJ} from Eq (109), Eq (115) can be solved for the c_i coefficients. Using these coefficients in Eq (113), $\Delta V_0(r)$ may be calculated. From this, a new $V_0^0(r)$ is obtained.

$$V_0^0(r) \text{ (new)} = V_0^0(r) \text{ (old)} + \Delta V_0(r) \tag{116}$$

Then using the new $V_0^0(r)$, the calculation is repeated to obtain new energy eigenvalues. Again, the calculated E_{vJ}^0 are compared with the experimental term values $T(v,J)$ for agreement. If the agreement is not acceptable, the process is repeated.

Elaboration upon the specific numerical calculations
to solve Eqs (106) through (116) is postponed until the dis-
cussion of Vidal's routine for performing the IPA calculations.

III Computer Programs

A computer program called DUNCON has been developed
to generate spectroscopic constants. DUNCON is presented
in Appendix A. The program generates the constants by
separate least-squares fits and provides for the merging of
the separate fits in a weighted manner as previously
described. A description of the program, a listing with a
sample fit and instruction on how to use it are contained in
Appendix A.

A second program, provided by C. R. Vidal of the Max-
Planck Institute for Exterrestriche Physik, West Germany,
has provisions for the generation of potential energy curves
by the Rydberg-Klein-Reese (RKR) method and adjustments of
those curves by the inverted perturbation approach (IPA).
The IPA routine adjusts the potential energy curve so it is
consistent with the Shroendinger wave equation. A copy of
the program with a sample problem, a description of the
program, and instructions on using the program are included
in Appendix B.

The DUNCON program and the RKR-IPA program may be used
in a variety of combinations to generate constants and
potential energy curves. Presented in Fig III-1 is a flow
diagram describing the logic used in applying these programs
in this work.

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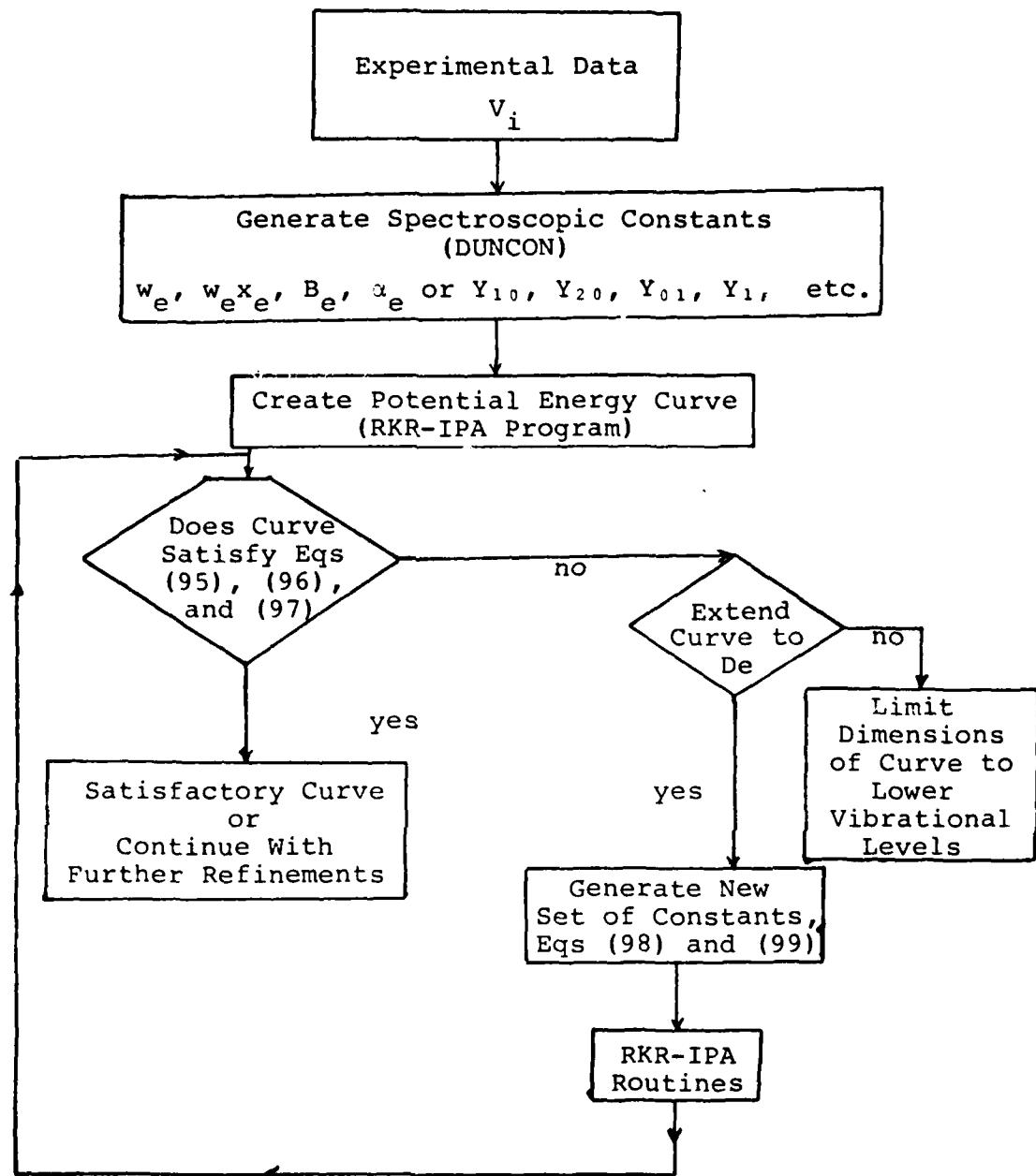
Fig III-1. Flow Diagram for Creation of Potential Energy Curves

DUNCON is used to generate spectroscopic constants by performing least-squares fits to the experimental data. These constants are then used as inputs to the RKR-IPA program. This program produces an RKR curve which is then adjusted by the IPA portion of the program.

Several options are available in the use of the RKR-IPA routines. The RKR routine can be used independently of the IPA routine. The range over which the curve is generated can be restricted to low vibrational energy levels or extended to the dissociation energy. If limited to small vibrational numbers initially, the RKR-IPA routine may be used iteratively to generate new constants and extend the curve to the dissociation limit.

In this paper, after initially generating an RKR-IPA curve, the curve is evaluated according to the criteria of Leroy and Burns, Eqs (95), (96), and (97). If a satisfactory curve is obtained, the calculation is complete. If not satisfactory, then the constants are adjusted as previously described. A modified version of the program DUNCON is used to perform the least-squares fit necessary to produce these constants. The constants are then again input into the RKR-IPA routine. The process is repeated until a satisfactory curve is obtained.

Programs demonstrating the use of DUNCON and the RKR-IPA programs are presented in Appendices A and B. Results of applying the program to the lead-oxide molecule are presented in the following chapter.

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IV. Analysis of Spectroscopic Data
for Lead-Oxide

This chapter contains the results of an analysis of spectroscopic data for lead-oxide (PbO). The program DUNCON was used to obtain spectroscopic constants for the X, a, b, A, B, and D electronic states of PbO. Constants from published literature were used to generate potential energy curves using the IPA-RKR routine. The potential energy curve for the ground state of lead-oxide was extended almost to the dissociation limit using the extension techniques and the RKR-IPA routine.

The experimental data of three investigations was reduced using DUNCON to yield spectroscopic constants. The data from these investigations is presented in Table IV-5. Two of the investigators, Glessner and Synder (Refs 19; 42), obtained least-squares fits, but did not have the computer routines necessary to generate error estimates and merge the data in a weighted-correlated manner. Their data is reduced, error estimates obtained, and merged using DUNCON. Lead-oxide data produced by Linton and Broida (Ref 33) is reduced using DUNCON and the A-X and a-X data is merged. Also, the results of all three investigations is merged using DUNCON. The results of reducing the data of each investigator for each transition separately is presented in Table IV-1. This

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data is then merged in several combinations. The constants resulting from these mergings are presented in Table IV-2. Presented in Table IV-3 are the unmerged and merged estimates for the D-X transitions. The D-X data is merged with other data in a separate fit to prevent its large variance from degrading the constants for the other transitions. Finally, the merged results of Glessner and Snyder's data, are compared in Table IV-4 with the best previous published values available.

The constants presented in columns I and II of Table IV-1 are not identical to those reported by the original investigators. When transforming their experimental data from angstroms to wavenumbers, they did not make corrections for the index of refraction of air as previously discussed. The constants listed in column III of Table IV-1 are also different from the values reported by Linton and Broida. For the A-X transition, they listed only their new band head data. They used data of other researchers to generate their constants. Their published constants are included in Table IV-4. The constants for the a-X transition of column III, Table IV-2 are also slightly different from those reported by Linton and Broida. Presumably, the slight difference arises from the difference in weighting schemes used in this report and that used by Linton and Broida.

TABLE IV-1

Constants from Separate Least-Squares Fits
for Each Electronic Transition (cm^{-1})

Electronic Transition	Constant	Source of Experimental Data		
		I Glessner	II Snyder	III Linton and Broida
a–x	Te	[10.03] 16021.54(2.81)	[9.875] 16021.68(2.59)	[6.310] 16023.12(1.38)
	We'	482.93(1.26)	484.51(1.09)	481.831(0.438)
	We'Xe	2.814(0.170)	2.970(0.146)	2.4590(0.0432)
	We"	719.36(2.19)	722.785(0.961)	720.166(0.469)
	We"Xe"	3.067(0.455)	3.712(0.105)	3.4600(0.0462)
b–x	Te	[2.035] 16336.43(6.08)^2		
	We"	428.98(1.46)		
	We'Xe	−0.944(0.114)		
	We"	722.00(1.92)		
	WeXe	3.554(0.193)		
A–X	Te	[41.70] 19846.0(25.8)	[33.07] 19858.52(6.88)	[4.817] 19864.79(2.38)
	We'	453.5(18.5)	446.30(4.92)	443.31(1.12)

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TABLE IV-1--Continued

Electronic Transition	Constant	Source of Experimental Data		
		I Glessner	II Snyder	III Linton and Broida
	We'Xe'	2.04(2.74)	0.479(0.8632)	0.443(0.146)
	We"	715.7(11.3)	724.69(2.93)	720.933(0.374)
	We"Xe"	2.80(1.58)	4.012(0.390)	3.5334(0.0239)
B-X	Te	[52.02]	[64.63]	
	We'	22290.9(10.3)	22286.22(9.06)	
	We'Xe'	495.70(4.34)	483.00(8.13)	
	We"	2.22(1.39)	-1.07(1.71)	
	We"	731.52(6.99)	721.11(3.85)	
	We"Xe"	5.06(1.11)	3.532(0.477)	

[1] The quantities in brackets are the variances of the least-squares fits (Eq (14)). Errors reported in parenthesis re one standard deviation. Column I contains least-squares fit to data produced by Glessner (Ref 19). Column II constants are based upon data produced by Snyder (Ref 42). Column III constants are the results of performing least-squares to data published by Linton and Broida (Ref 33).

[2] The constants for b-x were obtained by combining the data observed by Glessner and Synder.

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TABLE IV-2

Merged PbO Constants (cm-1)[1]

Electronic State	Constant	Source of Experimental Data		
		I Merging of Glessner and Snyder Data	II Merging of Linton and Broida Data	III Merging of Glessner, Snyder, Linton, and Broida Data
a	Te	16021.51(1.69)	16024.06(1.16)	16023.16(1.80)
	We'	484.239(0.808)	481.800(0.439)	481.488(0.769)
	We'Xe'	2.949(0.109)	2.4595(0.0434)	2.4339(0.0818)
b	Te	16335.44(2.89)		16331.83(4.77)
	We'	428.43(1.21)		428.34(2.27)
	We'Xe	-0.99552(0.0983)		-1.014(0.186)
A	Te	19856.22(3.31)	19864.11(2.14)	19860.04(3.13)
	We'	447.88(3.50)	443.39(1.12)	445.32(1.83)
	We'Xe'	1.013(0.6007)	0.446(0.145)	0.655(0.249)
B	Te	22282.80(3.67)		22280.52(7.08)
	We'	489.50(2.63)		489.79(5.25)
	We'Xe'	0.149(0.363)		0.225(0.720)
X	We"	721.905(0.620)	720.736(0.244)	720.890(0.395)
	We"Xe"	3.5900(0.0683)	3.5201(0.0171)	3.5316(0.0292)

TABLE IV-2--Continued

Electronic State	Constant	Source of Experimental Data		
		I Merging of Glessner and Snyder Data	II Merging of Linton and Broida Data	III Merging of Glessner, Snyder, Linton, and Broida Data
Variance of Fit		1.0248	1.008	4.076

[1]Column I is the result of merging with DUNCON the separate fits in Columns I and II of Table IV-1.
Column II is the result of merging the separate fits in Column III of Table IV-1.
Column III is the result of merging all separate fits in Table IV-1 with DUNCON.
Errors reported in parenthesis are one standard error.

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TABLE IV-3

Spectroscopic Constants for D-X Transition of PbO (cm^{-1})

Electronic State	Constant	Unmerged	Merged
		[322.3]	[4.19]
D	Te	29897.8(67.4)	30115.8(46.1)
	We'	490.0(30.8)	542.2(54.9)
	We'Xe'	-16.53(7.72)	-1.99(13.1)
X	We"	606.1(33.3)	720.989(0.401)
	We"Xe"	-8.32(3.53)	3.5312(0.0296)

Errors Reported in Parenthesis are One Standard Error

TABLE IV-4

Final Spectroscopic Constants for PbO[3]

Merged Constants	State	Te (cm⁻¹)	We (cm⁻¹)	WeXe (cm⁻¹)
This Study (Glessner and Snyder, Refs (19) and (42)	D	30115.8(46.1)	542.2(54.9)	-1.99(13.1)
	B	22282.80(3.67)	489.50(2.63)	0.149(0.363)
	AO+	19856.22(3.31)	447.88(3.50)	1.013(0.6007)
	2b	16335.44(2.89)	428.43(1.21)	-0.99552(0.0983)
	a	16021.51(1.69)	484.239(0.808)	2.949(0.109)
	x		721.905(0.620)	3.5900(0.0683)
Linton and Broida, Ref (33)	AO+	19862.6(1.5)	444.3(0.8)	0.54(0.12)
	al	16024.9(1.45)	481.5(0.7)	2.45(0.07)
	XO+		720.97(0.36)	3.536(0.025)
Bloomenthal, Ref (8)	D	30197.0	530.6	1.05
	B	22289.8	496.3	2.33
	X		722.3	3.73
Oldenborg, Dickensen and Zare, (Ref 36)	b	16379±430[1]		

[1]This value is based upon estimate by Oldenborg, Dickensen and Zare that the b state is 350±430 cm⁻¹ above the a state.

[2]Based upon six data points marked with asterisk in Table IV-7.

[3]Errors reported in parenthesis are one standard deviation.

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TABLE IV-5

Lead-Oxide Spectral Lines Assigned to the
D-X, B-X, A-X and a-X Transitions

Energy (cm^{-1})			Assignments	
Observed	Calculated	Obs-Calc	v',v"	Transition
Investigator: Snyder (Ref (42))				
28589.0	28607.2	-18.2	0,2	D-X
28432.8	28453.7	-20.9	1,3	D-X
27648.9	27625.7	23.2	2,5	D
27534.6	27501.3	33.3	3,6	D
27076.0	27075.5	00.5	1,5	D
26788.7	26829.9	-41.2	3,7	D
26555.3	26529.3	26.0	0,5	D
26394.0	26387.0	-3.0	1,6	D
24122.4	24120.5	1.9	4,0	B
23630.9	23632.5	-1.6	3,0	B
23146.1	23144.0	2.1	2,0	B
22640.3	22655.1	-14.8	1,0	B
22175.3	22165.8	9.5	0,0	B
21450.0	21452.0	2.0	0,1	B
20749.4	20745.2	4.2	0,2	B
20055.5	20045.5	10.0	0,3	B
19646.0	19645.5	0.5	2,5	B
19346.0	19352.9	-6.9	0,4	B
18772.8	18784.0	-11.2	3,7	B
17802.4	17806.7	-4.3	1,7	B
17631.6	17631.2	0.4	2,8	B
21054.4	21051.1	3.3	3,0	A
20166.0	20167.0	1.0	1,0	A
19811.0	19809.6	1.4	5,3	A

TABLE IV-5--<u>Continued</u>

Energy (cm-1)			Assignments	
Observed	Calculated	Obs-Calc	v',v"	Transition
19719.7	19723.0	-3.3	0,0	A
19456.0	19453.2	2.8	1,1	A
18996.1	19009.1	-3.0	0,1	A
18741.8	18746.4	-4.6	1,2	A
18293.3	18302.4	-9.1	0,2	A
17593.4	17602.7	-9.3	0,3	A
17338.3	17354.1	-15.7	1,4	A
16905.6	16910.0	-4.4	0,4	A
16224.6	16224.5	0.1	0,5	A
15315.4	15318.5	-3.1	1,7	A
19127.0	19137.9	-10.9	7,0	a
18679.9	18690.4	-10.5	6,0	a
18244.2	18238.2	6.0	5,0	a
17972.0	17976.6	4.6	6,1	a
17778.6	17781.0	-2.4	4,0	a
17520.3	17524.3	4.0	5,1	a
17320.6	17319.0	0.4	3,0	a
17064.6	17067.2	-2.6	4,1	a
16855.4	16852.1	3.3	2,0	a
16601.3	16605.2	-3.9	3,1	a
16384.7	16380.4	4.3	1,0	a
16135.6	16138.3	-2.7	2,1	a
15896.7	15898.4	-1.7	3,2	a
15662.6	15666.5	-3.9	1,1	a
15657.9	11650.4	7.5	4,3	a
15431.5	15431.5	0.0	2,2	a
15187.9	15189.9	-2.0	0,1	a
14958.6	14959.8	-1.2	1,2	a

TABLE IV-5--<u>Continued</u>

Energy(cm^{-1})			Assignments	
Observed	Calculated	Obs-Calc	v',v"	Transition
14732.2	14731.8	0.4	2,3	a
14481.2	14483.1	-1.9	0,2	a
14260.0	14260.1	-0.1	1,3	a
13782.7	13783.4	-0.7	0,3	a
13561.7	13567.4	-5.7	1,4	a
13353.6	13353.6	0.0	2,5	a
13083.0	13090.8	-7.8	0,4	a
12932.2	12932.5	-0.3	4,7	a
12874.0	12881.9	-7.9	1,5	a
12473.5	12470.5	3.0	3,7	a
12399.9	12405.2	-5.3	0,5	a
12266.0	12268.2	-2.2	4,8	a
12199.5	12203.3	-4.3	1,6	a
12065.8	12068.0	-2.2	5,9	a
11801.3	11806.1	-4.8	3,8	a
Investigator: Glessner (Ref (19))				
23629.2	23632.5	-3.3	3,0	B
23162.7	23144.0	18.7	2,0	B
22661.3	22655.1	6.2	1,0	B
21444.6	21452.0	-7.4	0,1	B
20745.1	20745.2	0.1	0,2	B
20042.7	20045.5	-2.8	0,3	B
19840.6	19842.2	-1.6	1,4	B
19453.7	19455.5	-1.8	3,6	B
18928.1	18924.9	3.2	6,9	B
18759.8	18761.3	-1.5	7,10	B

TABLE IV-5--<u>Continued</u>

Energy(cm^{-1})			Assignments	
Observed	Calculated	Obs-Calc	v',v"	Transition
21921.0	21929.9	-8.9	5,0	A
20163.9	20167.0	-3.1	1,0	A
19004.8	19009.1	-4.3	0,1	A
18299.6	18302.4	-2.8	0,2	A
17609.8	17602.7	7.1	0,3	A
16906.1	16910.0	-3.9	0,4	A
16219.6	16244.5	-25.0	0,5	A
15980.3	15990.0	-9.7	1,6	A
15762.6	15761.2	1.4	2,7	A
19127.7	19137.9	-10.2	7,0	a
18682.3	18690.4	-8.1	6,0	a
18237.9	18238.2	-0.3	5,0	a
17783.0	17781.0	2.0	4,0	a
17513.3	17524.3	-11.0	5,1	a
17316.7	17319.0	-2.3	3,0	a
17064.3	17067.2	-2.9	4,1	a
16852.8	16852.1	0.7	2,0	a
16603.2	16605.2	-2.0	3,1	a
16382.0	16380.4	1.6	1,0	a
16135.8	16138.3	-2.5	2,1	a
15898.0	15903.7	-5.7	0,0*	a
15668.5	15666.5	2.0	1,1	a
15433.4	15431.5	1.9	2,2	a
15193.0	15189.9	3.1	0,1	a
14963.5	14959.8	3.7	1,2	a
14732.4	14731.8	0.6	2,3	a
14483.8	14483.1	0.7	0,2	a
14261.4	14260.1	1.3	1,3	a

TABLE IV-5--<u>Continued</u>

Energy(cm-1)			Assignments	
Observed	Calculated	Obs-Calc	v',v"	Transition
13781.7	13783.4	-1.7	0,3	a
13564.1	13567.4	-3.3	1,4	a
13085.4	13090.8	-5.4	0,4	a
Investigator: Linton & Broida (Ref (33))				
22364	22367.4	-3.4	6,0	A
21930	21929.9	0.1	5,0	A
21654	21653.6	0.4	6,1	A
21494	21491.2	2.8	4,0	A
21221	21216.1	4.9	5,1	A
20949	20946.8	2.2	6,2	A
20777	20777.3	-0.3	4,1	A
20245	20247.1	-2.1	6,3	A
20069	20070.6	1.6	4,2	A
20168	20167.0	1.0	1,0	A
19366	19370.9	-4.9	4,3	A
19117	19117.0	0.0	5,4	A
18679	18678.2	0.8	4,4	A
17994	17992.7	1.3	4,5	A
17083	17081.5	1.5	5,7	A
14483	14880.9	2.1	3,9	A
14440	14439.5	0.5	2,9	A
14229	14230.7	-1.7	3,10	A
14217	14210.1	6.9	0,8	A
13998	13996.8	1.2	1,9	A
13789	13789.3	-0.3	2,10	A
13585	13587.5	-2.5	3,11	A
13390	13391.4	-1.4	4,12	A

TABLE IV-5--<u>Continued</u>

Energy (cm^{-1})			Assignments	
Observed	Calculated	Obs-Calc	v',v"	Transition
13201	13201.1	-0.1	5,13	A
13347	13346.6	0.4	1,10	A
13146	13146.1	-0.1	2,11	A
12951	12951.3	-0.3	3,12	A
12761	12762.3	-1.3	4,13	A
12580	15279.1	0.9	5,14 ·	A
12511	12509.9	1.1	2,12	A
12323	12322.3	0.7	3,13	A
12141	12140.3	0.7	4,14	A
11964	11964.2	-0.2	5,15	A
20448	20450.9	-2.9	10,0	a
20022	20018.1	3.9	9,0	a
19582	19580.4	1.6	8,0	a
19307	19304.2	2.8	9,1	a
19139	19137.9	1.1	7,0	a
18877	18866.6	10.4	8,1	a
18691	18690.4	0.6	6,0	a
18597	18597.5	0.5	9,2	a
18431	18424.0	7.0	7,1	a
18236	18238.2	-2.2	5,0	a
18160	18159.8	0.2	8,2	a
17977	17976.6	0.4	6,1	a
17782	17781.0	1.0	4,0	a
17526	17524.3	1.7	5,1	a
17317	17319.0	-2.0	3,0	a
17272	17269.8	2.2	6,2	a
17067	17067.2	-0.2	4,1	a
16854	16852.1	1.9	2,0	a

TABLE IV-5--<u>Continued</u>

Energy (cm^{-1})			Assignments	
Observed	Calculated	Obs-Calc	v',v"	Transition
16819	16817.6	1.4	5,2	a
16609	16605.2	3.8	3,1	a
16386	16380.4	5.6	1,0	a
16361	16360.4	0.6	4,2	a
16140	16138.3	1.7	2,1	a
16117	16117.9	0.9	5,3	a
15902	15898.4	3.6	3,2	a
15668	15666.5	1.5	1,1	a
15662	15660.7	1.3	4,3	a
15434	15431.5	2.5	2,2	a
15423	15425.2	-2.2	5,4	a
15191	15189.9	1.1	0,1	a
14961	14959.8	1.2	1,2	a
14734	14731.8	2.2	2,3	a
14510	14506.1	3.9	3,4	a
14485	14483.1	1.9	0,2	a
14286	14282.5	3.5	4,5	a
14261	14260.1	0.9	1,3	a
14071	14061.1	9.9	5,6	a
13828	13820.5	7.5	3,5	a
13784	13783.4	0.6	0,3	a
13569	13567.4	1.6	1,4	a
13355	13353.6	1.4	2,5	a
13146	13142	5.2	3.6	a
13092	13090.9	1.1	0,4	a
12884	12881.9	2.1	1,5	a
12667	12675.1	1.9	2,6	a
12407	12405.2	1.8	0,5	a

TABLE IV-5--<u>Continued</u>

Energy(cm^{-1})			Assignments	
Observed	Calculated	Obs-Calc	v',v"	Transition
12006	12003.6	2.4	2,7	a
11807	11806.1	0.9	3,8	a
11728	11726.7	1.3	0,6	a
11534	11531.9	2.1	1,7	a
11341	11339.3	1.7	2,8	a
11149	11148.8	0.2	3,9	a
11057	11055.3	1.7	0,7	a
10869	10867.5	1.5	1,8	a
10498	10498.6	-0.6	3,10	a
10391	10390.9	0.1	0,8	a
10212	10210.2	1.8	1,9	a

*Later reassigned as the "(3,2) a-X" transition.

Examination of Table IV-1 reveals values of w_e for the X-state ranging from 715.7 to 731.5 cm^{-1}. DUNCON permits the merging of the data listed in Table IV-1 in a weighted-correlated least-squares fashion.

The results of the merging are presented in Table IV-2. Error limits for w_e of the X-state are reduced from a maximum standard error of ±11.3 cm^{-1} to ±0.620 cm^{-1} when the data in columns I and II of Table IV-1 are merged. The results are presented in column I, Table IV-2.

Column II, Table IV-2 contains the smallest error estimate for the constants of the a-, A-, and X-electronic states. The variances for the merged fits of columns I and II are similar, 1.0248 and 1.008, respectively. But when the data in columns I and II are merged to yield column III, Table IV-2, the estimated *variance of the fit and, in many cases,* the standard errors of the individual constants increase. Examination of (columns I and II) the a- and X-states reveals term electronic energies, T_e , with error limits of comparable magnitude which do not overlap. Because of this, when merged, the error limits reflect the equal weighting of the "almost significant" differences and, hence, the increased error limit reflects a bias in one or both of the data sets.

Column III of Table IV-2 reflects the most conservative error estimate of the three columns in Table IV-2. It is also based upon the largest quantity of data.

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In reporting constants, a researcher may be tempted to manipulate the constants of the ground state and report the constants obtained from the least-squares fits for the upper state. For example, if a routine for merging fits is not available, one might average the constants for the ground state or obtain a weighted average based upon the error estimates. The temptation then is to report the averaged ground state constants and the upper state constants obtained from the original least-squares fits. Reporting constants in this fashion is undesirable for two reasons. First, the constants reported in this manner will not faithfully reproduce the experimentally observed data. Second, a better estimate of the ground state has been obtained. This new estimate of the ground state constants should, in turn, be used to ascertain how well the upper state constants are known. This can be done by removing (adding) the energy contributions of the ground state from the experimental data and performing a least-squares fit to obtain the upper state constants. These new upper state constants and the average ground state constants should provide an accurate reproduction of the experimental data and an accurate set of constants for the generation of potential energy curves. The approach just described is not necessary if a routine such as DUNCON is available for merging data. Even though it is available, the use of DUNCON to form a merged fit may not be desirable

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if large quantities of data are involved and the ground state constant has already been well defined.

Often the data merged from different investigators may contain different experimental values for the same assignment (v',v"). If after using DUNCON to obtain the best estimate of the constants, one of the experimental values agrees with the fit and the other does not, then one might remove the poorer data point and perform the fit again. This approach should be used with caution.

Presented in Table IV-4 are the constants obtained by merging the experimental data of Glessner and Snyder. Presented for comparison are results published by other researchers.

The data used to produce the constants of Tables IV-1 and IV-2 is presented in Table IV-5. The calculated values of Table IV-5 were obtained using the constants of column III, Table IV-2 and Table IV-3 for the D state.

The D-state constants were obtained in a separate merged fit from that used to obtain the other constants because of their large error. The values reported by Bloomenthal (Ref 8) produced a better fit for his data; hence, his constants are the preferred constants.

The B-state constants reported by Bloomenthal provide a better fit to his data than the constants reported here fit the B data listed in Table IV-5. This statement must be modified slightly. Bloomenthal did not provide "observed-

calculated" values for all the data he listed. Hence, these values may not have been included in his estimate of the constants.

The A-state constants reported in Table IV-4 provide a reasonable agreement with those reported by Linton and Broida (Ref 33). The reported constants are based upon the merging of data reported by Glessner and Snyder.

The small a-state constants reported in Table IV-4 rival those reported by Linton and Broida in accuracy. Table IV-2 shows that the merged data of Glessner and Snyder produces constants with error limits of magnitude comparable to that reported by Linton and Broida.

The ground state (x) constants reported in Table IV-4 agree well with those reported by Linton and Broida. The merging of Glessner's and Snyder's data resulted in constants for the X-state with significantly smaller errors than those obtained in separate fits of their data.

The discussion of the b-state data was reserved until last, because they were obtained by making reassignments of many transitions that were published in previous works.

The b-state constants listed in Table IV-1, column I are based upon the six assignments marked by asterisks in Table IV-7. The assignments were made by Glessner and Snyder (Refs 19; 42) based upon the works of Kurylo, et.al. (Ref 31). The variance of the constants in Table IV-2 is remarkably

small considering that only six data points with five constants were used yielding a degree of freedom of one. A review of Kurylo's tentative assignments and tentative assignments made by Oldenborg, Dickson, and Zare (Ref 36) show a much greater difference between the observed and calculated values than would be expected from the constants of Table IV-1.

Using the b-state constants of Table IV-1, new assignments were made for the experimental data which had been marked as belonging to the b-X transition by Kurylo and Oldenborg. It was possible to make new assignments for 29 of 34 observed values which had been reported as belonging to the b-state. Twenty-six of those were used in a least-squares fit to generate new b-state constants. DUNCON was used to perform separate least-squares fits to the data of Snyder and Glessner, and to the data of Kurylo and Oldenborg. Then DUNCON was used to merge the results of these fits. A copy of the program with the results is presented in Appendix A.

The resulting b-state and X-state constants are presented in Table IV-6. The 26 assignments used to obtain the constants are listed in Table IV-7. The "observed-calculated" values are presented for comparison with those of the original investigators. For the 26 values used in the new fit, a standard error of +10.5 cm was obtained. For the 15 values which the investigators reported "observed-calculated" values, their standard error was +47.4 cm. It should be noted

TABLE IV-6

Spectroscopic Constants for b-X
Transition for Lead Oxide

State	Te	We	WeXe
b	16325.1(11.2)	430.99(2.47)	-0.757(0.165)
X		721.41(4.35)	3.700(0.441)

that this error was due to uncertainties in the assignments and not the quality of the data.

The second part of Table IV-7 contains those values which were published as b-X transitions for which no assignments had been made at the time the fit was performed. After the new constants were calculated, assignments were made for three more b-X transitions.

The new assignments presented in this paper were made without access to the raw spectral data and, hence, information concerning the relative intensities of each transition. It is also probable that some of the assignments of the transitions to the b-state are incorrect. For example, the last value of Table IV-7, an experimentally observed value of 15672 cm^{-1} was assigned as a b-X transition. This value corresponds closely with the value of 15662 cm^{-1} observed by Linton and Broida and assigned to the a-X transition series.

TABLE IV-7

Lead-Oxide Spectrum for the b-X Transition

	This Work			Original Investigator	
Assignment	Observed (cm^{-1})	Calculated (cm^{-1})	Obs-Calc	Assignments	Obs-Calc
(14,1)	21643	21659.8	-16.8	(12,0)[O]	
	21636			(12,0)[K]	-24
(13,1)	21200	21207.6	- 7.7	(11,0)[O]	
(10,1)*	19869.8	19860.2	9.6	(10,1)[G]	4
(7,1)	18515	18526.3	-11.3	(5,0)[K]	-15
(3,0)	17488.4	17483.1	5.3	(3,0)[S]	- 5.5
(4,1)	17212	17206.1	5.9	(2,0)[K]	13
(7,3)	17108	17120.5	-12.5	(8,4)[K]	56
(2,0)	17033	17047.5	-14.5	(5,2)[K]	-75
(5,2)	16915	16938.0	-23.0	(1,0)[K]	-62
(3,1)	16773	16769.0	4.0	(1,0)[K]	16
(1,0)	16614	16613.5	- 0.5	(4,2)[K]	50
(4,2)	16488	16499.5	-11.5	(2,1)[K]	3
(7,4)	16434	16428.7	5.3	(10,5)[K]	67
(17,11)	16297	16292.4	4.6	(0,0)[K]	-18
(14,9)	16215	16214.1	0.9	(3,2)[K]	- 5
(3,2)*	16066.8	16062.4	4.4	(3,2)[S]	- 5.7

TABLE IV-7--Continued

	This Work			Original Investigator	
Assignment	Observed (cm^{-1})	Calculated (cm^{-1})	Obs-Calc	Assignments	Obs-Calc
(13,9)	15773	15762.0	11.0	(2,2)K	- 5
(2,2)	15623	15627.0	- 4.0	(0,1)K	22
(3,3)	15363	15363.2	- 0.2	(1,2)K	28
(9,7)*	15281.9	15285.4	- 3.5	(9,7)S	- 6.1
(3,4)	14687.8	14671.4	15.6	(3,4)S	8.4
(8,8)	14180.1	14178.5	1.6	(8,8)S	- 2.2
(0,4)	13367.30	13369.4	- 2.1	(0,4)S	10.5
(1,5)*	13117.5	13117.4	0.1	(1,5)S	5.9
(1,6)*	12440.1	12440.4	- 0.3	(1,6)S	- 7.4
(3,8)*	11968.9	11978.2	- 9.3	(3,8)S	- 8.9
	20786			(10,0)O	
	20354			(9,0)O	
	19923			(8,0)O	
(19,5)	21169	21161.4	7.6	(11,0)K	58
	20338			(9,0)K	24
	19904			(8,0)K	37

TABLE IV-7--Continued

	This Work			Original Investigator	
Assignment	Observed(cm^{-1})	Calculated (cm^{-1})	Obs-Calc	Assignments	Obs-Calc
(18,12)	16108	16618	-10	(6,4)^K	-52
(17,12)	15672 or 15662	15660	12	(5,4)^K a(4,3)$^{L\&B}$	-43

*These are the six transitions used to obtain the b-state constants of Table IV-1, column I.

    O – Oldenborg (Ref 36)

    S – Snyder (Ref 42)

    G – Glessner (Ref 19)

    K – Kurylo (Ref 31)

    L&B – Linton and Broida (Ref 33)

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This concludes the discussion of program DUNCON and the results of its application to lead-oxide. Only a small portion of the PbO data available was used in the present analysis. Rotational data, if used, should increase the quality of the constants. A more extensive evaluation of the literature data with the selective discarding of "erroneous" data points should yield better constants.

Lead-Oxide RKR-IPA Curves

To demonstrate the use of the RKR-IPA program, the X-, a-, and A-states were selected for evaluation. Curves were drawn for the X-, a-, and A-states using the results of the RKR routine alone or using the combined RKR and IPA routine (RKR-IPA curve). The resulting potential energy curves are presented in Fig. IV-1 for the X-, A-, and the a-states. For the A-state, the curve presented in Fig. IV-1 is an RKR curve, while for the X- and a-states, they are RKR-IPA curves. The RKR and IPA results are presented for the X- and a-states in Tables IV-8 and IV-9, respectively. The RKR data for the A-state is presented in Table IV-10. The constants used to generate these curves for each state is presented in Table IV-11.

The ultimate use of a potential should be to predict what transitions should occur. A sophisticated analysis would involve the calculation of Franck-Condon factors from the wave functions resulting from the solution of the Schroedinger wave

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A–
State

$v'' = 0$ Te
19862.6
cm^{-1}

a–
State

$v'' = 0$ Te
16024.9
cm^{-1}

X–
State

$v' = 0$

Internuclear Separation, Angstroms
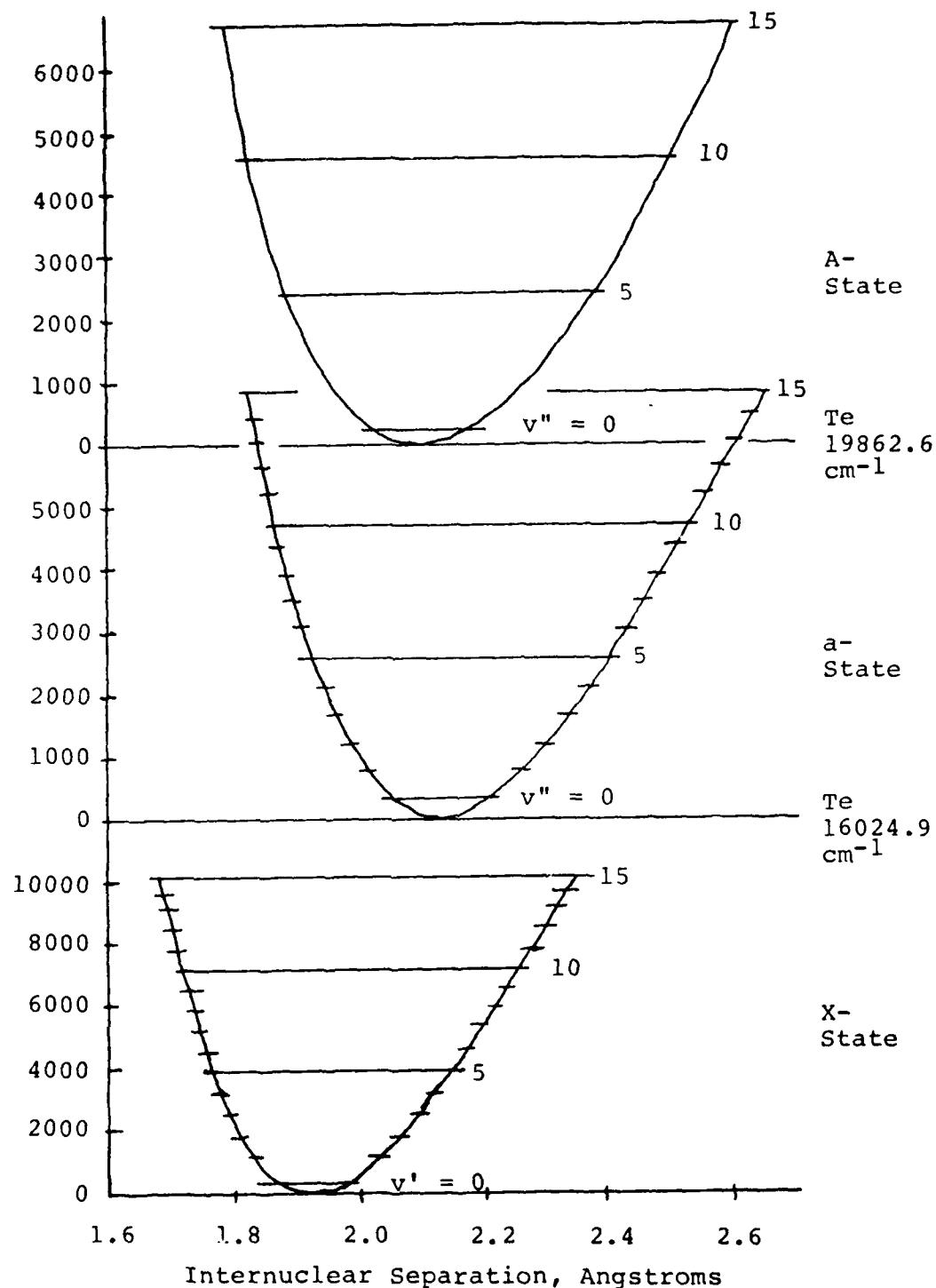
Fig IV-1.   Potential Energy Curves for Lead-Oxide
X, a, and A Electronic States

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TABLE IV-8

RKR and IPA Potential for Ground State of Lead-Oxide

V	RKR			IPA			
	$Gv(cm^{-1})$	$R-(\overset{\circ}{A})$	$R+(\overset{\circ}{A})$	$Gv(cm^{-1})$	$R-(\overset{\circ}{A})$	$R+(\overset{\circ}{A})$	$Bv(cm^{-1})\times100$
-½		1.921					
0	359.62	1.868	1.980	359.918	1.867	1.979	30.687
1	1073.52	1.832	2.027	1073.901	1.831	2.027	30.469
2	1780.34	1.809	2.062	1780.716	1.808	2.062	30.256
3	2480.10	1.790	2.092	2480.445	1.791	2.092	30.048
4	3172.78	1.775	2.118	3173.120	1.776	2.119	29.844
5	3858.39	1.762	2.143	3858.743	1.763	2.144	29.645
6	4536.93	1.751	2.167	4537.299	1.752	2.168	29.452
7	5208.40	1.740	2.189	5208.773	1.741	2.190	29.264
8	5872.79	1.731	2.211	5873.161	1.732	2.212	29.082
9	6530.11	1.722	2.231	6530.471	1.723	2.236	28.905
10	7180.36	1.714	2.251	7180.713	1.715	2.253	28.731
11	7823.54	1.706	2.271	7823.891	1.707	2.273	28.557
12	8259.65	1.699	2.291	8459.997	1.700	2.292	28.378
13	9088.68	1.693	2.311	9089.028	1.693	2.311	28.192
14	9710.64	1.686	2.330	9711.015	1.686	2.330	27.998
15	10325.53	1.680	2.349	10326.059	1.680	2.349	27.796

$Y_{00} = 0.0233501$ (RKR)

$Y_{00} = 0.37952$ (IPA)

TABLE IV-9

RKR and IPA Potential for the a-State of Lead-Oxide

V	RKR			IPA			
	$Gv(cm^{-1})$	$R-(\mathring{A})$	$R+(\mathring{A})$	$Gv(cm^{-1})$	$R-(\mathring{A})$	$R+(\mathring{A})$	$Bv(cm^{-1}) \times 100$
-½		2.122					
0	240.13	2.075	2.172	240.23	2.054	2.192	25.163
1				716.87	2.011	2.250	24.988
2				1188.55	1.982	2.293	24.822
3				1655.34	1.960	2.329	24.658
4				2117.24	1.942	2.363	24.495
5	2574.13	1.928	2.394	2574.24	1.925	2.392	24.328
6				3026.34	1.911	2.421	24.157
7				3473.56	1.899	2.448	23.979
8				3915.90	1.887	2.457	23.795
9				4353.34	1.877	2.501	23.607
10	4785.63	1.868	2.528	4785.85	1.868	2.527	23.419
11				5213.45	1.859	2.552	23.236
12				5636.23	1.850	2.576	23.060
13				6054.34	1.842	2.600	22.893
14				6467.82	1.834	2.624	22.729
15	6874.63	1.827	2.647	6876.59	1.827	2.648	22.562

$Y_{00} = 1.5566 \times 10^{-5}$

$Y_{00} = 0.16759$

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TABLE IV-10

RKR Potential for the A-State of Lead-Oxide

V	$G_v (cm^{-1})$	R-$\overset{\circ}{A}$	R+$\overset{\circ}{A}$
0.0	222.30	2.025	2.168
2.5	1328.32	1.937	2.288
5.0	2427.60	1.890	2.367
7.5	3520.12	1.856	2.432
10.0	4605.90	1.829	2.491
12.5	5684.92	1.807	2.546
15.0	6757.20	1.788	2.597

$$Y_{0} = 0.28500$$

TABLE IV-11

Input Constants and Data Used to Generate
Potential Energy Curves

Constants	State		
	X	a	A
Te^*	0.0	16024.9(1.45)	19862.6(1.5)
Y_{10}^*	720.97(0.36)	481.5(0.70)	443.3(0.8)
Y_{20}^*	- 3.536(0.025)	- 2.45(0.07)	- 0.54(0.24)
Y_{01}	0.307519**	0.252(0.10)*	0.2588**
Y_{11}	$- 1.9167 \times 10^{-3}$**	$- 1.6761 \times 110^{-3}$#	1.4×10^{-3}**
Y_{02}	2.2×10^{-7}**	2.2×10^{-7}##	3.3×10^{-7}**

Mass : Oxygen - 1.5994 amu; Lead - 207.19 amu.

*Source: Linton and Broida (Ref 33).

**Source: Suchard (Ref 45).

#Source: Calculated from Linton and Broida's Y_{01} using Eq (104).

##Source: Used X-state value for a-state Y_{02}. The a-state Y_{02} should be calculated according to Eq (104′). The error due to this substitution should be small.

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equation. But, it is possible to arrive at certain conclusions without calculation of the Franck-Condon factors. For example, examination of the a-state and X-state curves show that no overlap exists between the "v´=0" energy level for the a-state, and "v"=0" for the X-state. This indicates that such a transition is classically forbidden. In Table IV-5, a transition observed at 15898 cm had been assigned to the a-X (0,0) transition. Reevaluation showed that the 15898 band head should be the a-X (3,2) transition. Both assignments were acceptable within the error limits of fit. The relative positioning of the potentials indicate that only the (3,2) transition is possible. The calculated value for the a-X (3,2) transition is 15898.4 cm^{-1}.

The next step should be the generation of a new set of constants using the formulas for G_v and B_v and the newly obtained energy eigenvalues G_v and B_v values generated by the IPA routine. This technique was applied to the ground state IPA potential of Table IV-8. From this, the following constants were generated for the ground state:

$$Y_{10} = 720.991(0.058) \text{ cm}$$
$$Y_{20} = 3.5357(0.00479)$$

The calculation of new values for the rotational constants Y_{01} , Y_{11} , etc., from B_v was not performed.

The calculations using only Vidal's RKR-IPA method were halted at this point. Attempts to extend the curves to the dissociation limit "in one jump" produced a potential

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which diverged as the curve approached the dissociation limit (see Fig IV-2). Not having data for vibrational levels above about $v=15$, the iterative techniques of gradually extending the curve, as discussed by Vidal and Stawalley (Ref 43), were not attempted. They used the IPA method to improve the RKR curve at lower levels, and then on successive trials, extended the curve slowly to the dissociation limit.

The reader is referred to Vidal's works listed in the Bibliography and in Appendix C for further information concerning the generation of new constants and the extension of potential curves to the dissociation limit using the IPA routine.

This completes the discussion of the use of the RKR-IPA program by itself to generate potential curves. The next section presents use of the RKR-IPA technique in conjunction with Leroy's extension techniques to produce a potential energy curve which extends to the dissociation limit.

Extension of the X-State Lead-Oxide
Potential Energy Curve to the
Dissociation Limit, D_e

The potential energy curve for the ground state of lead-oxide was selected as the likely candidate for extension to the dissociation energy, D_e . This selection was based upon the fact that the constants for the ground state have the smallest standard errors.

The vibrational constants of Linton and Broida were selected as starting values because of their small error
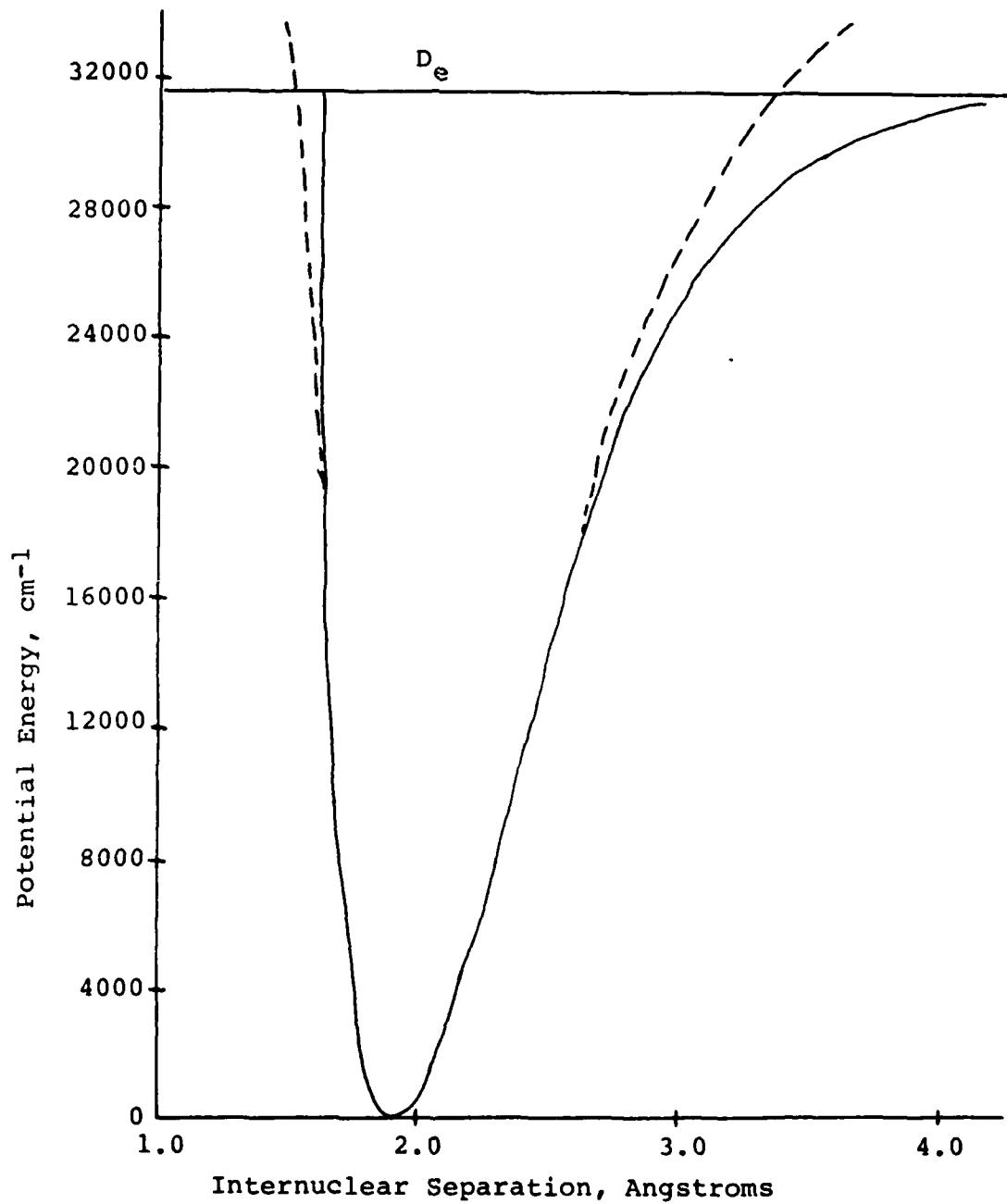
Fig IV-2.   Lead-Oxide X-State Potential Energy Curves

limits. The creation of potential energy curves also requires the knowledge of rotational constants. The rotational constants were selected from Suchard (Ref 45). Table IV-12 contains the original constants and the final set of constants used in extending the curve to the dissociation limit.

The method prescribed by Leroy was used. Linton and Broida's constants were used to generate a set of $G(v)$'s according to Eq (87) for $v=0$ to 15. A trial value was selected for Y_{40} and the other constants, Y_{30}, Y_{20}, and Y_{10} were solved for by performing a least-squares fit to the value obtained from Eq (98). Program DUNCON was modified to perform the fit. The process was repeated until the criterion of "$\Delta Gv+\frac{1}{2} = 0$" at D_e was satisfied.

Suchard's constants were used to generate a set of B_v's for $v=0$ to 15 according to Eq (93). A trial Y_{21} was selected and new Y_{01} and Y_{11} constants were obtained from a least squares fit to the values calculated by Eq (99).

The new vibrational constants and rotational constants were used as the inputs for the RKR-IPA program. The process of adjusting the rotational constants was repeated until the criteria expressed in Eqs (95), (96), and (97) were satisfied.

The last set of constants calculated are presented in Table IV-12 as the extended constants. The complete numerical results of the IPA-RKR routine are presented in Appendix B. The "Final Set of Turning Points," as output by the IPA routine was used to create the potential curve (solid line)

TABLE IV-12

**Constants Used to Extend the Lead-Oxide X-State
Potential Energy Curve to the
Dissociation Limit, D_e**

Constants	Original Values	Extended Values
Y_{10}	720.97(0.36)	721.062849
Y_{20}	-3.536	-3.57101904
Y_{30}		$3.85076374 \times 10^{-3}$
Y_{40}		-1.29×10^{-4}
Y_{01}	0.307519	0.30726775
Y_{11}	-1.9167×10^{-3}	-1.7667×10^{-3}
Y_{21}		-1.5×10^{-5}
Y_{02}	0.22×10^{-6}	0.22×10^{-6}

$$D_e = 31570 \pm 410. \ cm^{-1}$$

in Fig IV-2 which satisfies the dissociation criteria. The
dashed line in Fig IV-2 is the RKR curve, as defined by the
original constants of Linton and Broida, and Suchard. It
should be noted that the constants, as presented in Table
IV-12, will only produce the curve in Fig IV-2 when input
into an RKR-IPA routine. Examination of the "Final Set of
Turning Points" yields a minimum inner turning radius of
about 1.62 angstroms for vibrational quantum numbers from
v=33 to v=69. Examination of the turning points for the
initial "Potential Generated by RKR," listed at the beginning
of the RKR-IPA program output in Appendix B, shows RMIN
turning points as small as 1.54 angstroms for v=74. For
v=69, the last vibrational quantum number investigated by the
IPA routine, the RKR program returned an RMIN of 1.59 ang-
stroms. This decreasing value in RMIN indicates that the
left branch of the curve would diverge just as shown by the
dashed line on the left-hand side in Fig IV-2. The turning
points of the RKR potential were of sufficient quality that
the IPA program was able to correct the potential to yield
the solid curve of Fig IV-2. In this work, the procedure
described above, was the final one used; however, continued
refinements are possible by the use of the RKR-IPA program.
The next step should be to take the $G(v)$ $[U(R)]$ and
$B(v)$ $[BV*100]$ values as output by the IPA program and per-
form a least-squares fit to obtain a new set of Y_{n0} and Y_{n1}
constants. These, in turn, would be used as input for the

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constants from the experimental data and calculating the

higher $Y_{n+,n+}$ constants.

The convergence of the IPA routine became very sensitive as the "sought for value" of the last vibrational constant was approached. For the example, the IPA routine would not converge when values of $Y_{21} = -1.25 \times 10^{-5}$ or $Y = 1.75 \times 10^{-5}$ were used. The program would converge for values of Y_{21} larger and smaller than these, but the shape of the resulting curve diverged from the desired shape. An indication of the convergence of the IPA routine may be obtained by looking at the next to the last output of the IPA-RKR program, "The Summary of Errors of the Inverted Perturbation Approach."

Due to the fact that the "Final Set of Turning Points" fluctuates about 1.62 angstroms and the potential is increasing asymptotically along 1.62 angstroms, multiple potential energies are presented for the same RMIN turning point value. Thus, when searches are performed using a turning point radius value [XXX] as in DO-loop 55 of POTTAB, and PLYNN called from this loop, the routine stops at the first value satisfying the requirement [XXX]<X(J) (Subroutine PLYYN). The end result is that potential energies corresponding to turning points of magnitude of less than about 1.62 angstroms in the "Final Potential" should not be accepted as valid without close inspection. Improved constants and successive iterations of the RKR-IPA routine may remove this discrepancy.

V. Summary and Recommendations

The programs and techniques necessary to transform molecular spectra for diatomic molecules into potential energy curves have been presented and described in detail. The program DUNCON performs least-squares fits to separate data sets and then merges them in a weighted-correlated manner based upon the variances of the separate fits to yield spectroscopic constants. The RKR-IPA program presented first calculates "semi-classical" turning points based upon spectroscopic constants. It then adjusts the resulting RKR potential through an inverted perturbation technique to yield a potential energy curve whose energy eigenvalues are in best agreement with the model of a vibrating-rotating diatomic molecule as specified by the Schroedinger wave equation and with the experimentally observed data. The routing also calculates the wave functions for the potential energy curve.

Techniques were presented for extending potential energy curves to their dissociation limit when experimental data does not permit such an extension by straightforward application of the RKR technique.

Using DUNCON, constants for the a-X, A-X, B-X, and D-X transitions were calculated from experimental data. The results are presented in Tables IV-1, IV-2, and IV-3. The calculated values agree well with published values for these states.

A new set of assignments was made for b-X transi-
tions. The new constants calculated for the b-state are
presented in Table IV-6, and the new assignments are in Table
IV-7. The new assignments and constants produced a fit with
a standard error of 10.49 cm^{-1} versus 47.9 cm^{-1} for the
previous published assignments.

Recommendations

1. The use of Leroy's technique for extending a curve
to its dissociation limit in conjunction with the RKR-IPA
routine should be tested upon a potential energy curve whose
shape is known and for which experimental data is available
all the way up to the dissociation energy. If the technique
produces a curve and energy eigenvalues consistent with a
curve based upon experimental data then, the validity of the
method will be confirmed.

2. This technique for extending curves might be
further verified by applying it to two different states; for
example, a- and b-states of lead-oxide, whose dissociation
energies are the same. The coincidence of their potential
energy curves at large separations should serve to verify
both the extension technique and the quality of the constants
used in construction of the curves.

3. A complete investigation of all published data
using DUNCON should produce a better set of constants for
lead-oxide. This is particularly true for cases where two
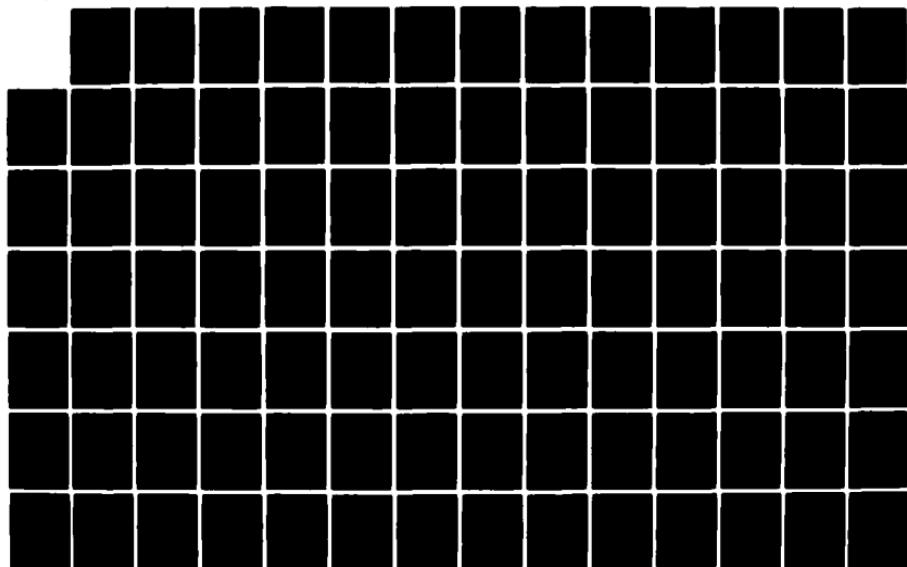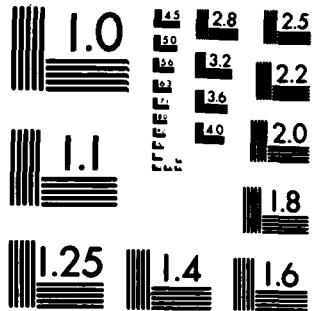
MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

investigators have given different energy levels for the same transition. The judgment as to which data is the more accurate should be based upon the constants produced by DUNCON.

4. Constants obtained from a least-squares fit should be reported as a group. If not, care should be taken to report how the constants were obtained.

5. The reassignments made for the b-X transitions should be evaluated by an investigator with access to data specifying the relative intensities of the experimental data. These were not available for the assignments made in this work.

Also, the b-state constants should be reevaluated using a more accurate set of X-state constants as opposed to those obtained from the least-squares fit of the b-X data. By fixing the value of the X-state constants, it may be possible to obtain a positive $w_e x_e$ for the b-state. Having a positive $w_e x_e$, then Eq (102) and Tellinghuisen's method for constructing a potential energy curve might be used. Alternatively, Eq (101) might be applied. From the potential energy curve, it might be possible to determine what transitions are more probable. Some information along these lines can be obtained by assuming a similarity between the a-state potential and estimating the position of the b-state curve relative to the a-state curve.

6. Vidal made use of the RKR-IPA routine to improve RKR curves for low energies and then used these improved

curves to extend the curves in small increments to higher energy levels. This technique has not been pursued and warrants further investigation. The RKR-IPA routine could even be used to improve constants for low energy levels, i.e., small "v", prior to using them in the previously described extension technique. Both techniques warrant further investigation.

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Appendix A

Program DUNCON

The following section contains the program DUNCON.
The program has provisions for obtaining separate least-
squares fits to separate data sets and then merging the
resulting constants in a weighted-correlated fashion based
upon the variances and covariances of the original separate
fits.

Presented first is a written description of the
program and instructions on how to use the program. Follow-
ing that is a listing of the program with a sample output.

Merged Least-Squares Spectroscopic
Constants Program

Program DUNCON is structured so the user can generate a least-squares fit to several different groups of data which have different standard errors and then merge the fits to obtain a weighted, correlated linear-least squares fit as described in the previous discussion on least-squares fits (Refs 2 and 3). DUNCON is written in Fortran V. A copy of DUNCON follows in this appendix.

The user must set up the model which will be used to fit his spectroscopic data, input the data, dimension the arrays used in his program, and call the subroutines WAVNUM, CONST, MATEQ, VECEQ, MATINV, and MERCN to obtain a merged least-squares fit. In turn, these routines call on a package of matrix manipulating routines (Ref 13) contained in the subroutine MATMULT.

Program DUNCON

The user has complete freedom in structuring this portion of the program. To perform a least-squares fit, the user must choose a model to represent his data. For data representing transitions between electronic states, the following is a typical model using Dunham coefficients (Ref 18):

$$\nu = T_e' + Y_{10}' + Y_{20}' - Y_{10}'' - Y_{20}'' \qquad (117)$$

where ν is the frequency of the transition expressed in units of cm^{-1}. As previously described, a series of transitions

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(ν) may be represented in matrix notation as:

$$\nu_k = X_k B_k + \varepsilon_k \qquad k = 1,2,3 \tag{118}$$

where ν is a column matrix made of experimentally determined wavelengths or wavenumbers:

$$\nu = \begin{bmatrix} \nu_1 \\ \nu_2 \\ \vdots \\ \nu_n \end{bmatrix} \tag{119}$$

The X matrix is made up of the $v'+1/2$, $(v'+1/2)$, $v''+1/2$, and $(v''+1/2)$ terms:

$$X = \begin{bmatrix} 1 & v_1'+1/2 & (v_1'+1/2)^2 & v_1''+1/2 & (v_1''+1/2)^2 \\ 1 & v_2'+1/2 & (v_2'+1/2)^2 & v_2''+1/2 & (v_2''+1/2)^2 \\ \vdots & & & & \\ 1 & v_n'+1/2 & (v_n'+1/2)^2 & v_n''+1/2 & (v_n''+1/2)^2 \end{bmatrix} \tag{120}$$

This X matrix is calculated in lines 18-28 of the subroutine CONST. As the specific model chosen to represent spectroscopic data may vary, the user must define this section of CONST.

The β column matrix (vector) will contain the constants of the least-squares fits.

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$$\beta = \begin{bmatrix} Te' \\ Y_{10}' \\ Y_{20}' \\ Y_{10}'' \\ Y_{20}'' \end{bmatrix} \qquad (121)$$

To operate the program, the user must input the following data:

1. $\underline{\nu}$—the experimentally determined energy of transition expressed in either angstroms (A) or wavenumbers (cm^{-1}). In the sample program in this appendix, ν is called ANUx, where the small "x" represents the additional characters necessary to identify a specific group of data. This convention is continued throughout the discussion in this section.

2. $\underline{v'}$—the vibrational quantum number associated with the upper state and referred to as QV1x in the program. It should be entered as a decimal.

3. $\underline{v''}$—the vibrational quantum number associated with the lower state and referred to as QV2x in the program. It should be entered as a decimal.

NOTE: the values of ANUx, QV1x, and QV2x for each observed transition must be associated with each other by subscripts. (The subscript is placed in parenthesis and the subscript must start with "0".) For example:

ANUx(0),QV1x(0),QV2x(0)

ANUx(1),QV1x(1),QV2x(1)

ANUx(2),QV1x(2),QV2x(2)

etc.

4. $\underline{N}$--the number of constants minus one to be calculated in the initial least-squares fit. For the model in Eq (117), N should be defined as follows: $N = 5 - 1 = 4$.

5. $\underline{Mx}$--corresponds to the number of experimental values to be included initially in a data set for least-squares fitting prior to the merging step.

6. $\underline{MM}$--corresponds to the total number of constants minus one which are generated in the initial least-squares fits for each of the independent data sets. For example, if the calculation is for two different transitions, i.e., A-X, B-X, and, as in Eq (1), five constants are to be calculated then $MM = 2*5 - 1 = 9$.

7. $\underline{NM}$--the number of constants to be obtained in the merged least-squares fit.

8. $\underline{XM(0:MM,0:NM)}$--the coefficient matrix which relates the redundant variables obtained from independent least-squares fits to the desired final set of variables. It controls the merging of the constants obtained in the separate least-squares fits to yield the merged weighted, correlated least-squares constants by the following formula:

$$\beta^M = (X^T \theta I^{-1} X)^{-1} \quad X^T \theta I^{-1} y \qquad (122)$$

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For a problem involving five constants for each of two electronic transitions, the XM matrix would be of size 14x5 and contain the elements as follows:

State

		A			B		X		
	Te	Y'_{10}	Y'_{20}	Te	Y'_{10}	Y'_{20}	Y''_{10}	Y''_{20}	← Merged Constant
Te	1	0	0	0	0	0	0	0	
Y'_{10}	0	1	0	0	0	0	0	0	Elements Pertaining to AX Transitions
Y'_{20}	0	0	1	0	0	0	0	0	
Y''_{10}	0	0	0	0	0	0	1	0	
Y''_{20}	0	0	0	0	0	0	0	1	
Te	0	0	0	1	0	0	0	0	
Y'_{10}	0	0	0	0	1	0	0	0	Elements Pertaining to B-X Transitions
Y'_{20}	0	0	0	0	0	1	0	0	
Y''_{10}	0	0	0	0	0	0	1	0	
Y''_{20}	0	0	0	0	0	0	0	1	

XM =

↓

Constants from Independent Least-Squares Fit

Fig A-1. Coefficient Matrix XM

9.   <u>THETAI(0:MM,0:MM)</u>--this matrix is made by merging the variance-covariance matrices obtained from each of the independent least-squares fits. The details of its construction will be provided in the discussion of the subroutine MATEQ. The user must initially fill the matrix with zeros. The matrix has $(MM+1)^2$ elements. For example, if MM=9, then the statement, DATA THETAI (100*0D0) will initialize the matrix.

This concludes the data input required of the user. The only tasks remaining are the assembly of dimension statements and construction of statements in the main portion of the program to execute the least-squares and merging routines.

The sequence of statements required to perform a least-squares fit for each set of data are as follows:

        CALL WAVNUM

        CALL CONST

        CALL MATEQ

        CALL VECEQ

In the following section, the statement names and their arguments are listed along with a brief description of the routine.

WAVNUM(ANUx,Mx)

This subroutine converts data contained in the array ANUx(0:Mx) from angstroms to wavenumbers invacuo (cm^{-1}) by means of a correction for the index of refraction of air (Refs 7 and 21). ANUx is, as described above, an array of

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the Mx experimental values for one group of data. NOTE: If ANUx is entered as wavenumbers, this statement is omitted.

CONST(ANUx,QV1x,QV2x,BETx,THETx,Xx,Xtx,XTXx,XTXXTx,XBx,

   ANUXBx,CVRCx,Mx,N)

This routine does the work of obtaining minimum variance least-squares constants. It solves the matrix equation as outlined below:

$$\nu = X\beta + \epsilon \tag{124}$$

$$\beta = (X^T X)^{-1} X^T \nu \tag{125}$$

$$\sigma^2 = (\nu - X\beta)^T (\nu - X\beta)/fm \tag{126}$$

$$\theta = \sigma^2 (X^T X)^{-1} \tag{127}$$

The correspondence between the arguments for CONST and these equations are as follows including the dimensions required for the arrays: $ANUx(0:Mx) = \nu$

$QV1x(0:Mx)$ and $QV2x(0:Mx)$: These entries are the quantum mechanical vibration numbers which are for the upper (v′) and lower (v″) states respectively, and are used to generate the Xx matrix as previously described.

$Xx(0:Mx,0:N) = X$: This matrix is generated by CONST in lines 18-28, as dictated by the user and by the model chosen to represent the data.

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$XTx(0:N,0:Mx) = X^T$: This matrix is the transpose of matrix X and is generated by the subroutine TRNSPZ called from CONST.

$XTXx = first(X^TX)$, then $(X^TX)^{-1}$: This matrix is the product of X^T and X formed by the subroutine MATMLT. The matrix is then replaced by its inverse by the routine MATINV.

$XTXXTx(0;n,0:M) = (X^TX)^{-1}X^T$: This matrix is the product of the inverse of the first matrix times the transpose of the second.

$BETx(0:N) = (X^TX)^{-1}X^T\nu$: This column matrix (vector) contains the least-squares estimate of the constants in Eq (1). It is formed by multiplying the matrix XTXXTx times the vector, ν , using the routine MATVEC.

$XBx(0:Mx) = X\beta$: This column matrix is the product obtained from the subroutine VECVEC. It is the calculated estimate of the original experimental values based upon the constants obtained from the least-squares fit of the experimental data.

$ANUBx(0:Mx) = (\nu - X\beta)$: This column matrix (vector) contains the differences between the measured and calculated values of wavelength for a given data set. The calculation is performed by the routine VECSUB.

$VARINZ = \sigma^2 = (\nu - X\beta)^T (\nu - X\beta)/f_m$: VARINZ is a scalar and is the estimated variance of the least-squares fit.

The variance is given in the output of the program. f_m is the degree of freedom, $Mx - N$. VARINZ is calculated in the routine CONST.

THETx$(0:N,0:N) = \theta = \sigma^2 (X^TX)^{-1}$: THETx is the variance-covariance matrix for the calculated constants. Estimates of the variance for the constants are contained on the diagonal with off diagonal elements being the covariances. The matrix is obtained from the product of the scalar, σ^2, and the matrix, $(X^TX)^{-1}$, using the routine SCAMAT.

CVRCx$(0:N,0:N)$: This matrix is generated by CVRCOR which is called from CONST. It contains three types of data.

1. Above its diagonal it contains the same covariances of the constants as in THETx.

2. The diagonal contains the estimate of the standard error of each of the constants.

3. The elements below the diagonal are the correlation coefficients associated with the constants. The coefficients are calculated by the following formula:

$$C = \theta_{ij} / (\theta_{ii}\theta_{jj})^{\frac{1}{2}} \qquad (129)$$

where θ_{ij} are the elements of the matrix θ. Since the matrix is symmetric, the procedure of reporting variances for the top half and covariances for the bottom half is sufficient. The results are printed in the program output.

This completes the description of the arrays required for the least-squares fit of one group of data. If it is

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necessary to perform a least-squares fit on several sets of
data and merge them to obtain a correlated, weighted, least-
squares estimate of the constants, then the MATEQ and VECEQ
routines are used.

The merged least-squares calculation is based upon:

$$y = X\beta^M + \varepsilon \tag{130}$$

where the known values obtained from the previous least-
squares fits of the experimental data are the y and X matrices
and

$$y = \begin{bmatrix} Te \\ Y'_{10} \\ Y'_{20} \\ Y''_{10} \\ Y''_{20} \\ Te \\ Y'_{10} \\ Y'_{20} \\ Y''_{10} \\ Y''_{20} \end{bmatrix} \tag{131}$$

etc.

and X is the XM matrix as defined in the input data section.
It relates the redundant values of y to the corresponding
members of β^M (Ref 3). β^M is the best estimate of the
constants obtained from the formula

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$$\beta^M = (x^T \theta I^{-1} x)^{-1} x^T \theta^{-1} y \qquad (132)$$

where θI is of the form

$$\theta I = \begin{bmatrix} \theta_1 & 0 & 0 \\ 0 & \theta_2 & 0 \\ 0 & 0 & \theta_3 \end{bmatrix} \qquad (133)$$

MATEQ(THETx,THETAI,N,N,MM,MM,x,x)

This routine inserts the variance-covariance matrices, the THETx's from each least-squares fit, into the matrix THETAI.

THETx(0:N,0:N) : As previously defined.

THETAI(0:MM,0:MM) = I : As previously defined.

The last two arguments for MATEQ, "x,x", determine where the smaller matrices are inserted into THETAI. The user must input these values (as integers). For the first group of data, "x,x" should be "0,0". If the number of constants determined in each of the separate least-squares fits is "N+1", then "x,x" for the second THETx inserted into THETAI is "2*(N+1),2*(N+1)"; third, "3*(N+1),3*(N+1)", etc. The end result is the placement of the THETx matrices into THETAI as depicted by Eq (133).

CALL VECEQ(BETx,YM,N,MM,x)

VECEQ performs a similar insertion of the constants BETx obtained in the separate least-squares fits into the

column matrix (vector) YM (y in Eqs (131) and (132)). The
dimensions of these two parameters are BETx(0:N), and YM(0:MM).

The "x" value is again an integer and entered by the
user. It corresponds to and is equal to the value used in
the MATEQ statement. In this manner, the estimated constants
and their variances are placed within the THETAI and YM
matrices so their correspondence is retained in the merging
calculations.

After the CALL WAVNUM through VECEQ statements have
been executed for each of the separate groups of experimental
data and the YM and THETAI matrices are loaded, the merging
of the spectroscopic constants can be carried out. To
accomplish this, the user must have constructed the XM matrix
as previously described. Then the following statements will
accomplish the merging:

     IPV = 0

     CALL MATINV

     CALL MERCN

CALL MATINV (THETAI,MM,MM,IPV)

This routine inverts the THETAI matrix. The routine
was obtained from the computer program by C. R. Vidal contained
in Appendix B.

CALL MERCN(XM,THETAI,YM,XTM,XTHM,XTHMX,XTXXTH,BETAM,XBM,YXBM,
       YXTH,THETAM,CVRCM,MM,NM)

This routine performs the calculations outlined in Eq (132) to yield a set of merged least-squared constants. MERCN estimates by the following formula, the variance to be obtained using the merged constants:

$$\sigma_m^2 = (y - X\beta^M)^T \theta I^{-1} (y - X\beta^M)/f_m \qquad (134)$$

It then calculates the variance-covariance matrix, θ^M, for the merged constants according to the following formula:

$$\theta^M = (X^T \theta I^{-1} X)^{-1} \qquad (135)$$

Listed next are the arguments of MERCN and their correspondence to the equations presented in other sections of the report.

XM(0:MM,0:MM) = X : In Eqs (130), (132), (134), and (135).

THETAI(0:MM,0:MM) = θI : Eqs (133), (134), and (135).

YM(0:MM) = y : Eqs (130), (131), (132), and (134).

XTM(0:NM,0:MM) = X^T : Eqs (132) and (135).

XTHM(0:NM,0:MM) = $X^T \theta I$: Eqs (132) and (135).

XTHMX(0:NM,0:NM) = first $(X^T \theta I^{-1} X)$ then $(X^T \theta I^{-1} X)^{-1}$: Eqs (132) and (135).

XTXXTH(0:NM,0:MM) = $(X^T \theta I^{-1} X)^{-1} X^T \theta I^{-1}$: Eq (132).

BETAM(0:NM) = β^M : Eqs (130), (132), and (134).

XBM(0:MM) = XβM : Eq (134).

YXBM(0:MM) = y - Xβ^M : Eq (134).

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$$YXTH(0:MM) = (y - X\beta^M)^T \theta I^{-1} \; : \; \text{Eq (134).}$$

$$THETAM(0:NM,0:NM) = \sigma^2 (X^T \theta I^{-1} X)^{-1} \; : \; \text{Eq (134).}$$

This is the variance-covariance matrix for the merged constants.

CVRCM(0:NM,0:NM): CVRCM is the matrix containing the covariances, standard errors, and the correlation coefficients of the merged constants with the structure the same as described for the separate least-squares fits.

Calculations are performed in the subroutines CONST and MERCN using a group of matrix and vector manipulation routines (Ref 13).

The output of the program consists of the following for each separate set of data.

1. A listing of the experimental input values ν, ν' and ν'' with the calculated value $X\beta$.

2. The variance of the fit.

3. The complete variance-covariance matrix.

4. The matrix containing the covariances, standard errors and correlation coefficients.

5. The constants for the upper and lower levels.

For the merged data, the merged constants, the variance of the fit and variance, covariance, standard errors, and correlation coefficients of the merged constants are printed.

```
1          PROGRAM DUNCON
2    C        DUN319, DUN317, DUN324, 10 DEC 82
3    C     IMPLICIT DOUBLE PRECISION (A-H,O-Z)
4    C        DIMENSIONING STATEMENTS FOR SNYDER-GLESSNER SMALL B-X
5    C        LEAD-OXIDE DATA
6          DIMENSION ANUA(0:9),QVA1(0:9),QVA2(0:9)
7          DIMENSION ABETA(0:4),THETA(0:4,0:4),XA(0:9,0:4),XTA(0:4,0:9)
8          DIMENSION XTXXTA(0:4,0:5),XBA(0:5),XTXA(0:4,0:4),ANUXBA(0:9)
9          DIMENSION CVRCA(0:4,0:4)
10   C        DIMENSION STATEMENTS FOR OLDENBERG, DICKSON, AND ZARE
11         DIMENSION ANUB(0:5),QVB1(0:5),QVB2(0:5)
12         DIMENSION ABETB(0:4),THETB(0:4,0:4),XB(0:5,0:4),XTB(0:4,0:5)
13         DIMENSION XTXXTH(0:4,0:5),XBB(0:5),XTXB(0:4,0:4),ANUXBB(0:5)
14         DIMENSION CVRCB(0:4,0:4)
15   C        DIMENSION STATMENTS FOR DATA OF KURYLO, ET.AL.
16         DIMENSION ANUC(0:15),QVC1(0:15),QVC2(0:15)
17         DIMENSION ABETC(0:4),THETC(0:4,0:4),XC(0:15,0:4),XTC(0:4,0:15)
18         DIMENSION XTXXTC(0:4,0:15),XBC(0:15),XTXC(0:4,0:4),ANUXBC(0:15)
19         DIMENSION CVRCC(0:4,0:4)
20   C        ARRAYS FOR MERGING 3 SEPARATE FITS
21         DIMENSION XM(0:9,0:4),THETAI(0:9,0:9),YM(0:9)
22         DIMENSION XTM(0:4,0:9),XTHM(0:4,0:9),XTHMX(0:4,0:4)
23         DIMENSION YXTH(0:4),THETAM(0:4,0:4),CVRCM(0:4,0:4)
24         DIMENSION XTXXTM(0:4,0:9),BETAM(0:4),XBM(0:9),YXBM(0:9)
25   C        DATA FOR SNYDER-GLESSNER
26         DATA ANUA/5716.500,6606.500,7030.200,7476.900,6222.300,
27        +6541.900,7621.300,8036.300,6352.700,5031.400/
28         DATA QVA1/300,300,800,800,300,900,100,100,300,1000/
29         DATA QVA2/600,400,800,400,200,700,500,600,300,100/
30   C        DATA FOR OLDENBERG
31   C          A=0
32   C      DATA FOR KURYLO
33   C        DATA IN INVERSE CENTIMTERS
34         DATA ANUC/2164300,2120000,1551500,
35        +1721200,1710200,1703300,1691500,1677300,
36        +1661400,1647700,1643400,1629700,1621500,1577300,
37        +1562300,1536300/
38         DATA QVC1/1400,1300,700,400,700,200,500,300,
39        +100,400,700,1700,1400,1300,200,300/
40         DATA QVC2/100,100,100,100,300,000,200,100,000,
41        +200,400,1100,900,900,200,300/
42   C        INITIALIZING MERGING MATRICES
43         DATA XM/100,4*000,100,5*000,
44        +100,4*000,100,5*000,
45        +100,4*000,100,5*000,
46        +100,4*000,100,5*000,
47        +100,4*000,10 /
48         DATA THETAI/100*000/
49   .       .
50   .
51         N=4
52         NA=9
53         NB=5
54         NC=15
55         NM=9
56         M=4
57   C        CALCULATION OF CONSTANTS FOR SNYDERS DATA
58         CALL WAVNUM(ANUA,NA)
59         CALL CONST (ANUA,QVA1,QVA2,ABETA,THETA,XA,XTA,XTXA,XTXXTA,
60        +XBA,ANUXBA,CVRCA,NA,N)
61         CALL MATEQ(THETA,THETAI,N,N,MM,MM,0,0)
62         CALL VECEQ(ABETA,YM,N,N,MM,0)
63   C        CALCULATION OF CONSTANTS FOR KURYLOS DATA
64         CALL CONST(ANUC,QVC1,QVC2,ABETC,THETC,XC,XTC,XTXC,XTXXTC,
65        +XBC,ANUXBC,CVRCC,NC,N)
66         CALL MATEQ(THETC,THETAI,N,N,MM,MM,5,5)
67         CALL VECEQ(ABETC,YM,N,N,MM,5)
68         IPV=1
69         CALL MATINV(THETAI,MM,MM,IPV)
70         CALL MERCH(XM,THETAI,YM,YTM,XTHM,XTHMX,XTXXTH,
71        +BETAM,XBM,YXBM,YXTH,THETAM,CVRCM,MM,NM)
72         END
```

```
 1              SUBROUTINE MATINV(A,N,M,IPV)
 2      C          REFERENCE:  OBTAINED FROM PROGRAM PREPARED BY C.R. VIDAL
 3      C          MATRIX INVERSION
 4      C          IPV.EQ.1:  NO SEARCH FOR PIVOT.  IPV.NE.1: SEARCH FOR PIVOT
 5              IMPLICIT DOUBLE PRECISION (A-H,O-Z)
 6              DIMENSION IPIVOT(0:63),INDEXR(0:63),INDEXC(0:63)
 7              DIMENSION A(0:N,0:M)
 8      C          ....................INITIALIZATION
 9        .
10              DO 20 J=0,N
11        20    IPIVOT(J) = 0
12              DO 500 I=0,N
13              IF (IPV.NE.1) GO TO 40
14               ICLM=I
15              GO TO 200
16      C          ...................SEARCH FOR PIVOT ELEMENT
17        40    AMAX=0.0
18              DO 105 J=0,N
19              IF (IPIVOT(J).EQ.1) GO TO 105
20      C          FOR UNSYMMETRIC MATRIX:  A(I,J).NE.A(J,I)
21              DO 100 K=0,N
22      C          FOR SYMMETRIC MATRIX:  A(I,J).EQ.A(J,I)
23      C          DO K=J,N
24              IF (IPIVOT(K).EQ.1) GO TO 100
25              IF (ABS(AMAX).GE.ABS(A(J,K))) GO TO 100
26              IROW=J
27              ICLM=K
 2              AMAX=A(J,K)
29       100    CONTINUE
30       105    CONTINUE
31              IPIVOT(ICLM)=IPIVOT(ICLM) + 1
32              INDEXR(I)= IROW
33              INDEXC(I)= ICLM
34      C          ......INTERCHANGE ROWS TO PUT PIVOLT ELEMENT ON DIAGONAL
35              IF (IROW.EQ.ICLM) GO TO 260
36        .
37              DO 200 L=0,N
38              SWAP= A(IROW,L)
39              A(IROW,L)=A(ICLM,L)
40       200   A(ICLM,L) = SWAP
41        .
42        .
43        .
44        .
45        .
46       260   PIVOT = A(ICLM,ICLM)
47              IF (N.GT.10) GO TO 330
48        .
49      C          ..................DIVIDE PIVOT ROW BY PIVOT ELEMENT
50       330   A(ICLM,ICLM) = 1.0
51              DO 350 L = 0,N
52       350   A(ICLM,L)=A(ICLM,L)/PIVOT
53        .
54        .
55        .
```

```
56     C        ...............REDUCE NCN-PIVOT ROWS
57     3.0   DO 550 L1 = 0,N
58           IF (L1.EQ.ICLM) GO TO 550
59           T = A(L1,ICLM)
60           A(L1,ICLM) = 0.0
61           DO 450 L= 0,N
62     450   A(L1,L) = A(L1,L) - A(ICLM,L)*T
63     .
64     .
65     .
66     550   CONTINUE
67           IF (IPV.EQ.1) RETURN
68     C        ...............INTERCHANGE COLUMNS
69           DO 710 I= 0,N
70           L= N-I
71           IROW = INDEXR(L)
72           ICLM = INDEXC(L)
73           IF (IROW.EQ.ICLM) GO TO 710
74           DO 705 K = 0,N
75           SWAP=A(K,IROW)
76     .
77           A(K,IROW) = A(K,ICLM)
78     705   A(K,ICLM) = SWAP
79     710   CONTINUE
80           RETURN
81           END
```

A-18

```
1          C        THE FOLLOWING ROUTINES PERFORM STANDARD MATRIX OPERATIONS
2          C        AND VECTOR OPERATIONS
3          •
4          •
5                   SUBROUTINE MATMLT(A,U,T,M,N,P)
6                   IMPLICIT DOUBLE PRECISION (A-H,O-Z)
7                   DIMENSION A(0:M,0:N),U(0:N,0:P),T(0:M,0:P),B(0:M,0:N)
8                   DIMENSION D(0:P1,0:P2)
9                   DIMENSION X(0:N),Y(0:N),Z(0:M),V(0:N,0:M),Z1(0:N)
10                  INTEGER I,J,M,N,C,P
11                  INTEGER P1,P2
12         •
13                  DO 1 I=0,M
14                  DO 1 J=0,P
15         1        T(I,J)=0D+0
16                  DO 2 I=0,M
17                  DO 2 J=0,P
18                  DO 2 K=0,N
19         •
20         2        T(I,J)= A(I,K)*U(K,J) + T(I,J)
21                  RETURN
22         •
23                  ENTRY VECSUB(X,Y,Z1,N)
24         C        THIS ROUTINE SUBTRACTS TWO VECTORS
25                  DO 3 I=0,N
26                  Z1(I)=X(I)-Y(I)
27         3        CONTINUE
28                  RETURN
29         •
30                  ENTRY MATVEC (A,X,Z,M,N)
31         •THIS ROUTINE MULTIPLIES A MATRIX TIMES A VECTOR YEILDING A VECTOR
32                  DO 5 I=0,M
33         5        Z(I)=0D+0
34                  DO 6 I=0,M
35                  DO 6 J=0,N
36         6        Z(I)=A(I,J)*X(J) + Z(I)
37                  RETURN
38         •
39                  ENTRY SCAVEC (S,X,Y,N)
40         •        THIS ROUTINE MULTIPLIES A SCALAR TIMES A VECTOR TO YEILD A VECTOR.
41                  DO 7 I=0,N
42         7        Y(I)=S*X(I)
43                  RETURN
44         •
45                  ENTRY SCAMAT (S,A,B,M,N)
46         •        ROUTINE MULTIPLIES A SCALAR TIMES A MATRIX
47                  DO 8 I=0,M
48                  DO 8 J=0,N
49                  B(I,J)=S*A(I,J)
50                  RETURN
51         •
52                  ENTRY VECVEC (X,Y,S,N)
53         •        THIS ROUTINE MULTIPLIES TWO VECTORS TOGETHER YEILDING A SCALAR
54                  S=0D+0
55                  DO 9 I=0,N
```

A-19

```
56              *        S= S + X(I)*Y(I)
57                       RETURN
58              *
59                       ENTRY VECMAT (Z,A,K,M,N)
60              C        THIS ROUTINE MULTIPLIES A VECTOR TIMES A MATRIX TO YEILD A VECTOR
61                       DO 10 J=C,N
62                       X(J)= CO+0
63                       DO 10 K=C,M
64              10       X(J)=X(J) + Z(K)*A(K,J)
65                       RETURN
66              *
67                       ENTRY TRNSPZ (A,V,M,N)
68              C        THIS ROUTINE TRANPOSES A MATRIX
69                       DO 14 I=C,M
70                       DO 14 J=0,N
71              14       V(J,I)=A(I,J)
72                       RETURN
73              *
74              *
75              *
76                       ENTRY CVRCOR(A,T,M,N,P)
77              C            THIS ROUTINE CREATES A MATRIX FOR PRINT OUT OF
78              C        STANDARD ERRORS, COVARIANCES, AND CORRELATION COEFFICIENTS OF
79              C        THE "CULMAN COEFFICIENTS".
80              *
81              *
82                       DO 15 I=C,M
83                       DO 15 J=0,M
84                       IF (I.LT.J) THEN
85                       T(I,J)=A(I,J)
86                       ELSE IF (I.EQ.J) THEN
87                       T(I,J)=DSQRT(A(I,J))
88                       ELSE IF (I.GT.J) THEN
89                       T(I,J)=A(I,J)/(DSQRT(A(I,I))*DSQRT(A(J,J)))
90                       END IF
91              15       CONTINUE
92                       RETURN
93                       ENTRY WAVNUM(X,N)
94              C            THIS ROUTINE CONVERTS WAVELENGTHS IN ANGSTROMS TO
95              C        WAVE NUMBERS(INVERSE CENTIMETERS).
96              C        WITH CORRECTION FOR INDEX OF REFRACTION OF AIR
97              C        REFERENCE:  R.T. BIRGE, PHYSICAL REVIEW, VOL. 60, 766-785(1941).
98                       DO 16 I=C,N
99                       WL = X(I)/1000.0D0
100                      XREF = 272.5D100 + 1.5453D0/WL**2D0 + 0.0215800/WL**4D0
101                      XREF = 1D0 + XREF/1D6
102             16       X(I) = 1D5/(WL*XREF)
103                      RETURN
104                      ENTRY MATEQ(A,C,M,N,P1,P2,K1,K2)
105             C            THIS ROUTINE TRANSFERS MATRIX A(M,N) INTO MATRIX C
106             C         - STARTING AT POSITION X(K1,K2)
107                      M2=K1+M
108                      N2=K2+N
109                      DO 17 I=K1,M2
110                      DO 17 J=K2,N2
111                      I2=I-K1
112                      J2=J-K2
113                      C(I,J)=A(I2,J2)
114             17       CONTINUE
115             17       CONTINUE
116                      RETURN
117             *
118             *
119                      ENTRY VECEQ(X,Z,N,M,P1)
120             C            THIS ROUTINE TRANSFERS MATRIX X(N) INTO VECTOR Z(M)
121             C         STARTING AT POSITION Z(P1)
122                      N2=N+P1
123                      DO 18 I=P1,N2
124                      I2=I-P1
125                      Z(I)=X(I2)
126             18       CONTINUE
127                      RETURN
128                      END
```

```
 1              SUBROUTINE CONST(ANU,QV1,QV2,BETA,THETA,X,XT
 2          *,XTX,XTXXT,XH,ANUXB,CVRC,M,N)
 3      C       THIS ROUTINES PERFORMS THE ACTUAL CALCULATION OF THE
 4      C       "DUNHAM MOLECULAR CONSTANTS."
 5              IMPLICIT DOUBLE PRECISION (A-H,O-Z)
 6              DIMENSION ANU(0:M),QV1(0:M),QV2(0:M)
 7              DIMENSION BETA(0:N),THETA(0:N,0:N)
 .              DIMENSION XT(0:N,0:M),X(0:M,0:N),XTX(0:N,0:N),XTXXT(0:N,0:M)
 .              DIMENSION XH(0:M),ANUXB(0:M),CVRC(0:N,0:N)
10              DOUBLE PRECISION L1
11              N2=N/2
12              N3=N2+1
13      C        THIS SECTION CALCULATES THE X MATRIX WHICH IS MADE UP
14      C        OF THE VIBRATIONAL AND/OR ROTATIONAL QUANTUM NUMBERS
15      C           WITH "V+1/2" AND "J*(J+1)" RAISED TO POWERS MAKING UP
16      C        THE X(I,J) TERMS.
17      *
1.              DO 2001 I = 0,M
19              DO 2000 L = 0,N2
20              L1 =L
21              L2 = L + N2 + 1
22              X(I,L)=(QV1(I)+0.5D0)**L1
23       2000 CONTINUE
24              DO 2002 L=N3,N
25              L1=L-N2
26              X(I,L)=-(QV2(I)+0.5D0)**L1
27       2002 CONTINUE
2.       2001 CONTINUE
29      C       CALCULATION OF CONSTANTS
30              CALL TRNSFZ(X,XT,M,N)
31              CALL MATMLT(XT,X,XTX,N,M,N)
32              IPV=0
33              CALL MATINV(XTX,N,N,IPV)
34              CALL MATMLT(XTX,XT,XTXXT,N,N,M)
35              CALL MATVEC(XTXXT,ANU,BETA,N,M)
36      C       CALCULATION OF VARIANCE OF ENERGY LEVEL.  OF IS DEGREES
37      C        OF FREEDOM.
3.              DF=1.0D+0/DBLE(M-N)
39              CALL MATVEC(X,BETA,XH,M,N)
40              CALL VECSUB(ANU,XB,ANUXB,M)
41              PRINT*," QV1   QV2   OBSERVED                   CALCULATED"
42              DO 996 I=0,4
43              PRINT 999 ,QV1(I),QV2(I),ANU(I),XB(I)
44        999 FORMAT (2X,F3.0,2X,F3.0,2X,F19.7,2X,F19.7)
45        996 CONTINUE
46              CALL VECVEC(ANUXB,ANUXB,STEMP,M,M)
47              VARINZ=STEMP*DF
4.              PRINT*," "," VARIANCE ",VARINZ
4.              PRINT*," ","VARIANCE COVARIANCE MATRIX ELEMENTS"
50              CALL SCAMAT(VARINZ,XTX,THETA,N,N)
51              DO 123 I=0,N
52              DO 123 J=0,N
53              PRINT*," ",I,J,THETA(I,J)
54        123 CONTINUE
55      C
```

A-21

```
56          C           THIS SECTION PLACES THE COVAIANCES ABOVE THE DIAGONAL
57          C           OF THE MATRIX "CVRC."  IT PLACES THE STANDARD ERRORS
58          C           FOR THE CONSTANTS ON THE DIAGONAL.  ITS CALCULATES THE
59          C           CORRELATION COEFFICIENTS AND PLACES THEM BELOW THE DIAGONAL.
60                      CALL CVRCCR(THETA,CVRC,M,N,N)
61                      PRINT *,"STANDARD ERROR(I=J), CORRELCOEFF(I>J),COVARIANCE(I<J)"
62                      DO 615 I=0,N
63                      DO 614 J=0,N
64          614  PRINT *,"  ",I,J,CVRC(I,J)
65          615  CONTINUE
66          C           PRINT OUT THE CONSTANTS FOR THE TWO ELECTRONIC STATES
67                      PRINT *,"1"
68                      PRINT *,"  ","VIBRATIONAL CONSTANTS FOR UPPER LEVEL"
69                      DO 2010 I=0,N2
70          2010 PRINT *,"  ",I,BETA(I)
71                      PRINT *,"  "
72                      PRINT *,"  ","VIBRATIONAL CONSTANTS FOR LOWER STATE"
73                      DO 2020 I=N3,N
74          2020 PRINT *,"  ",I,BETA(I)
75                      PRINT *,"1"
76                      END
```

A-22

```
1              SUBROUTINE MERGN(XM,THETAI,YM,XTM,XTHM,XTHMX,XTXXTH,           C
2             +BETAM,XBM,YXBM,YXTH,THETAM,CVRCM,M,N)                          C
3        C        THIS ROUTINE MERGES RESULTS TO OBTAIN A BEST ESTIMATE      C
4        C        OF THE SPECTOGRAPHIC CONSTANTS                             C
5              IMPLICIT DOUBLE PRECISION (A-H,Q-Z)                           C
6              DIMENSION XM(0:M,0:N),THETAI(0:M,0:M),YM(0:M)                  C
7              DIMENSION XTM(0:N,0:M),XTHM(0:N,0:M),XTHMX(0:N,0:N),XTXXTH(0:N,0:M
8             +)
9              DIMENSION BETAM(0:N),XBM(0:M),YXTH(0:M),THETAM(0:N,0:N)        C
10             DIMENSION YXBM(0:M)
11             DIMENSION CVRCM(0:N,0:N)                                      C
12        C        CALCULATE DEGREES OF FREEDOM AND DIVIDE INTO 1            C
13             DF=1D0/(M-1.)                                                 C
14        C        CALCULATE MERGED CONSTANTS                               C
15             CALL TRNSPZ(XM,XTM,M,N)                                       C
16             CALL MATMLT(XTM,THETAI,XTHM,N,M,M)                            C
17             CALL MATMLT(XTHM,XM,XTHMX,N,M,N)                              C
18             IPV=C                                                         C
19             CALL MATINV(XTHMX,N,N,IPV)                                    C
20             CALL MATMLT(XTHMX,XTHM,XTXXTH,N,N,M)                          C
21             CALL MATVEC(XTXXTH,YM,BETAM,N,M)                              C
22             PRINT*,' ',' MERGED CONSTANTS'                               C
23             DO 2500 I=0,N                                                 C
24       2500 PRINT*,' ',I,BETAM(I)                                          C
25        C        CALCULATE ESTIMATED VARIANCE OF MERGED FIT               C
26             CALL MATVEC(XM,BETAM,XBM,M,N)                                 C
27             CALL VECSUB(YM,XBM,YXBM,M)                                    C
28             CALL VECMAT(YXBM,THETAI,YXTH,M,M)                             C
29             CALL VECVEC(YXTH,YXBM,TEMP,M)                                 C
30             VARM=DF*TEMP                                                  C
31             PRINT*,' ','ESTIMATED VARIANCE OF MERGED FIT'                C
32             PRINT*,' ',' ',VARM                                          C
33        C        CALCULATE VARIANCE-COVARIANCE MATRIX                     C
34             CALL SCAMAT(VARM,XTHMX,THETAM,N,N)                            C
35             PRINT*,' ','VARIANCE-COVARIANCE MATRIX'                      C
36             DO 2510 I=0,N                                                 C
37             DO 2520 J=0,N                                                 C
38       2520 PRINT*,' ',I,J,THETAM(I,J)                                     C
39       2510 CONTINUE                                                       C
40        C        CALCULATE MATRIX CONTAINING STANDARD ERRORS,COVARIANCES, C
41        C        AND CORRELATION COEFFICIENTS.                            C
42             PRINT*,' ','STANDARD ERROR(I=J),COVARIANCE(I<J),CORRELATION ' C
43             PRINT*,' ','COEFFICIENTS(I>J)'                               C
44             CALL CVRCOR(THETAM,CVRCM,N,N,N)                               C
45             DO 2530 I=0,N                                                 C
46             DO 2540 J=0,N                                                 C
47       2540 PRINT*,' ',I,J,CVRCM(I,J)                                      C
48       2530 CONTINUE                                                       C
49             END                                                          C
```

QV1	QV2	OBSERVED	CALCULATED
3.	0.	17480.4535272	17427.5335259
3.	4.	14687.6345663	14602.0419301
8.	8.	14180.1271055	14175.5752521
0.	4.	13367.3042301	13367.6563264
3.	2.	16762.6475222	16072.9523207
9.	7.	15281.9128564	15247.3239519
1.	5.	13117.5451259	13118.5212743
1.	6.	12440.1462036	12437.6603405
3.	8.	11962.913857	11771.2336055
..	..	...7 /5...	19460.1576193

```
    VARIANCE   27.151-53047332.653554534E-6
VARIANCE COVARIANCE MATRIX ELEMENTS
 0 0 106.94377354765.9125035351...
 0 1 -24.8230352753.46196865374406
 0 2 1.4554806327130195364294161617
 0 3 29.72831467.2022265361505.4
 0 4 -3.039422069966105449561467204
 1 0 -24.8230052753.4613.66937.404
 1 1 9.65501194254124197450547072
 1 2 -.6937229501795163151594637059
 1 3 -5.33970877.53061435404753737
 1 4 .590342274.643A0529499515251
 2 0 1.4554806327130609534424041615
 2 1 -.6937229567951631515946370559
 2 2 .05767234A652256607.2H85234411
 2 3 .38231321661624.845298540695
 2 4 -.0423019804889164476142194149
 3 0 29.72831467.2022265361505985
 3 1 -5.33970877453061435484753746
 3 2 .383319216616244845298590701
 3 3 10.81036807796638908694347119
 3 4 -1.12878957131627680276969448
 4 0 -3.039422069966105449561467247
 4 1 .59034227886438C052949953525P
 4 2 -.0423019804399164476142194155
 4 3 -1.1287895713162789027696944d
 4 4 .12213769321157305347503C5532
STANDARD ERROR(I=J), COFRELCOEF(I>J),COVARIANCE(I<J)
 0 0 10.341362505246576035211769
 0 1 -24.8230052753046198865379406
 0 2 1.4554806327130L953642941617
 0 3 29.72831467A20222653615059H4
 0 4 -3.039422069966105945561467266
 1 0 -.815910954530275794487410141
 1 1 2.9419401493812347742904627b
 1 2 -.6937229567951631515946370509
 1 3 -5.33970877953061435484753739
 1 4 .590342278A6438052949953525251
 2 0 .747127709611386315065492160a3
 2 1 -.981902610730813605940460774
 2 2 .2491506794749013952524249366
 2 3 .332319216616249845298590605
 2 4 -.142301980489916447614219149
 3 0 .87432377173491561703855904876
 3 1 -.55203103496366779146370073766
 3 2 .494196969797379850867983291
 3 3 3.29791241944651072678435463
 3 4 -1.1287895713162788027696944B
 4 0 -.440985278A673F2339124252159
 4 1 .5741762142960882639117997520
 4 2 -.50402493719220773121211797e7
 4 3 -.9823537131591750531207061290
 4 4 .349482035620675435408365922
1
VIBRATIONAL CONSTANTS FOR UPPER LEVEL
 0 16312.026857295930565062947.3
 1 436.758636992113042910613P53
 2 .342474361766C864066190621136
0
VIBRATIONAL CONSTANTS FOR LOWER STATE
 3 716.1671616776270129315077451
 4 -2.958852346565066905015542633
1
```

QV1	QV2	OBSERVED	CALCULATED
14.	1.	21643.00.0000.	21645.5097295

```
     7.    1.        1+515.0380099          15517.1+031CC
     4.    1.        17212.C9C0004          17159.650656+
     7.    3.        1710/.0000000          17114.7119709
     2.    0.        17C33.CJ/7003          17C41.7C92C1C
     5.    2.        16515.C30CG0J          16+32.2+02129
     3.    1.        16773.00J0609+         1C763.6231663
     1.    0.        16614.09J003C          16C38.7402357
     4.    2.        1648+.6030003          16454.6631721
     7.    4.        16434.C3uC0C+          16424.837656?
    17.   11.        162+7.C300060          16390.24720C3+
    14.    3.        16215.0000003          16217.5145372
    13.    9.        15773.0Ju0300+         15765.5517442
     2.    2.        15623.G03000           15624.C777412
     3.    3.        15363.0J3000+          15361.1446271
   VARIANCE   H4.+4431372538094P947291303?
VARIANCE CGVARIANCE MATRIX ELEMENTS
0 0 69.99465547+927649720806+73C1
0 1 -1+.31936870326773573174471143
0 2 .96792810362089162866712156
0 3 .65620697069607106J[9103397+
0 4 .123530805+4028+421747521572
1 0 -16.31936970328773573174471143
1 1 12.73229754175751153517669951
1 2 -.74653467423555703119C447673
1 3 13.092649160149632195318C017+
1 4 -1.279461750170260156766400+7
2 0 .96792810379209516828667121557
2 1 -.74653467423557C03115J0447673
2 2 .04528314541565726386653C6071
2 3 -.7+444835680436296596856155+5
2 4 .C7998057754130129161458022767
3 0 .6562069706560710600+1J34C4
3 1 13.092649160149632163531+60172
3 2 -.79444835++043+296+9685615 5
3 3 24.7102B30124769760337850+3+
3 4 -2.2+7636234328C69729866C02+ +6
4 0 .125530805+4028+421747521565
4 1 -1.279461750170260156766400+7
4 2 .07998057754130129161458022766
4 3 -2.28763623432+C5972+666002+ 6
4 4 .2207719811172536061928726+64
STANDARD ERROR(I=J), CORRELCOEF(I>J),CGVARIANCE(I<J)
0 0 9.3603023557122412070489c695+
0 1 -13.319368+C326773573174471143
0 2 .96792810382085182366712156
0 3 .656206970696071066J5103397+
0 4 .124530905+4028+421747521572
1 0 -.51409438567182049+4160R2998
1 1 3.568234513279292779295364109
1 2 -.74653467423555703119C447673
1 3 13.092649160144632145316+017+
1 4 -1.27946175017C260156765400+7
2 0 .54406754945306601+234638625
2 1 -.+8316928349739265210A167776
2 2 .21279936793165+317666419827
2 3 -.7+444835H+043+296+96C+615 5
2 4 .07398057754130129161458022767
3 0 .01578992239197R275+73+377623
3 1 .734134120256676346115612043
3 2 -.75103213439325961+4752663+
3 3 4.97094387545031291091131+24
3 4 -2.28763623432+C5972+668C02P+6
4 0 .0327199980167+595012+4377435
4 1 -.76313573770611495+90+364143
4 2 .7+99157+23106246+470635+2343
```

```
4 4 .4.986379033061F5726542F117
1
VIBRATIONAL CONSTANTS FCP UPPER LEVEL
0 16321.336303470C816522543;11
1 429.36936958759635029493u772
2 .77476512225549496369511713
0
  VIBRATIONAL CCNSTANTS FCR LOWER STATE
  3 720.18064535671168402472235
  4 -3.788295160F6542335187A6514%
1
  MERGED CONSTANTS
0 16325.086001343072464A1323C19
1 430.2927387631366420+619323
2 .7571374657657726109729459-45
3 721.40646257dF90950566385459
4 -3.6996278567262031047966864R
ESTIMATED VARIANCE OF MERGED FIT
  4.68359860216323195620772275
VARIANCE-COVARIANCE MATRIX
0 0 126.363261426977672167649463
0 1 -14.88477840255399741747107-5
0 2 .6362666506363705995692942269
0 3 34.753641551821355656546556575
0 4 -3.107488121646273086137206858
1 0 -14.88477840255399741747107-5
1 1 6.0878552907272451612380749
1 2 -.382724311901454576640520447
1 3 .93164059915504454175352+962
1 4 -.1344963797590940558505111'1
2 0 .636266650636370555692'426C
2 1 -.382724311901454576640520447
2 2 .027177821794692233681551316
2 3 -.185417894407544335325907805
2 4 .023127104722574241157378833-1
3 0 34.753641551821355656546556575
3 1 .93164059915504454175352+952
3 2 -.185417894407544335325907cC7
3 3 18.89930811119657606228466534
3 4 -1.86325815351165674859706127
4 0 -3.10748812164827300-6137206g-
4 1 -.1344963797590540558505111h9
4 2 .023127104722574241157378836
4 3 -1.86325819351165674859706127
4 4 .134611060499614c5231459664505
STANDARD ERROR(I=J),COVARIANCE(I<J),CORRELATION
CCEFFICIENTS(I>J)
0 0 11.2411414645923690629616723
0 1 -14.884778402553957417471075
0 2 .63626665063637059956929426'
0 3 34.753641551821355656556575
0 4 -3.10744812164627303613720658
1 0 -.53666070F76110103277%425021
1 1 2.46735795755584964746h7-35622
1 2 -.3827.431190145457664052044
1 3 .93164059915044541753524962
1 4 -.13449637975909405585505111h91
2 0 .343337645134132079449334746
2 1 -.3409367134446912601553253479
2 2 .16485697375207462947274857
2 3 -.185417894407544335325907A63
2 4 .023127104722574241157378835-1
3 0 .71115939466862126d4164849-1
3 1 .086A5469370046457749A41321711
3 2 -.2587148566169295464156977774


3 4 -1.5632531635116587445706127
4 0 -.62663570E663A6074714531612
4 1 -.12356477270464253777744259
4 2 .311002243535114563+7573134
4 3 -.9715526233706d2323256t3a79=7
4 4 .44114743623625269962324128c
```

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Appendix B

RKR-IPA Program

The following section contains the RKR-IPA program as provided by C. R. Vidal.

Presented first is a written description of the program and instructions on the use of the program. Next, the original introductory comments by C. R. Vidal on the use of the program are presented.

Then a complete listing of the program and a sample output is presented.

Program Main (RKR-IPA Control)

Presented in the following section is a discussion
of the RKR-IPA program provided by C. R. Vidal (Ref 41).
The program MAIN contains a routine to perform RKR calcula-
tions and a routine to perform IPA calculations starting with
the potential obtained from the RKR program. The program
was originally written in Fortran IV to run on a CRAY-1
computer at the Max-Planck Institut fur Extraterrestrische
Physik, Garching, Germany. It has been modified slightly
to run on the CDC 6600 computer at the Air Force Institute
of Technology, Wright-Patterson AFB, Ohio. The program, as
presented in this appendix, is written in Fortran V. Comments
provided by Vidal at the front of his program are included.
PUNCH statements included by Vidal have been changed to
comment cards. Many of the formatting statements have been
changed from Hollerith editing to apostrophe editing formats.

Due to memory size constraints, 370 K octal, several
arrays were reduced in size. Arrays now sized (2403) were
originally sized (3601) in Vidal's program. Arrays sized
(11,2403) were originally (24,3601) in size.

As sized, the program required a field length of
211,600 octal to run. A core memory size of 360 K was used.
Maximum run times used for the RKR routine were less than 20
seconds. This involved the calculation of turning points
(RMIN, RMAX) for 128 different energy levels.

Run time for the combined RKR-IPA routine ranged from 160 seconds for the calculation of parameters covering the following ranges:

v, vibrational quantum energy levels; $v = 0$ to 69

J, rotational quantum energy levels; $J = 1$

Iterations of IPA routine; $n = 4$

Array sizes; 1001 of 2403 maximum

to a maximum run time of 1150 seconds for:

$v = 0$ to 70

$J = 2,6,10,14,17,20,21,23,28,30$

$n = 4$

Array sizes; 1001 of 2403 maximum

One change has been made in the logic of Vidal's program. In the function subroutine FUNC, line 37, the third line after statement label 70, was changed from:

IF (XX.GT.RAA) RETURN

to

IF (KK.EQ.1) RETURN

The consequences of and reasons for suggesting this change are presented in the discussion of FUNC.

The discussion of Vidal's program is divided into two subsections: first, the discussion of the RKR portions of his program and, then, a discussion of the IPA portion. Within each section, the discussion is started with the inputs required of the user. Then the logic of the program is

traced with explanations of the calculations and the sub-routines used.

Numerical RKR Calculations

This section starts with the inputs required to perform the RKR calculations. The card number, the name of the input and the format of the input is given. The word CARD is used if only one card is required. CARDSET is used if more than one card (line of data) may be required.

CARD 1

NAME: ITEST

FORMAT: Integer.

ITEST should be placed in column 1. If ITEST = 0, the program stops. If ITEST = 1, the program is executed.

CARD 2 and 3

NAME: IHEAD

FORMAT: Lines 1-72 of these two cards. These two cards contain the title to be printed at the top of the output. Relevant information that is suggested for the title includes the name of the molecule with the isotopes involved, the electronic state for which the calculations is performed, date, etc.

CARD 4

NAME: IIMS, ZMAS1, ZMAS2, ICODE

FORMAT: I4,2D16.9,32X,A4

IIMS must be 1 if the masses of the atoms are expressed in AMU's based upon the Carbon-12 scale and 2 if they are based upon the Oxygen-16 scale. ZMAS1 and ZMAS2 are the masses of the two atoms expressed in atomic mass units (AMU). The reduced mass of the two atoms may be entered in place of ZMAS1. If the reduced mass is used, ZMAS2 is left blank.

ICODE is the alphanumeric code used to describe the electronic state under investigation.

CARD 5

NAME: NDUN, JM(1), JM(2)...JM(NDUN)

FORMAT: 14I5

NDUN and JM specify the number of Dunham coefficients YDH and the order in which they will be read into the program.

CARDSET 6

NAME: YDH(1,1), YDH(2,1)...YDH(JM(2),1)
      YDH(1,2), YDH(2,2)...YDH(JM(2),2)

.

.

.

YDH(1,NDUN), YDH(2,NDUN)...

YDN(JM(NDUN),NDUN)

FORMAT: 4D18.9

These cards contain the Dunham coefficients
required as input for the RKR routine. The
READ statement is structured so that JM(I)
values of YDH(JM(I),I) are read in for
each value of I with I ranging from 1
through NDUN. For each new value of I,
the 1 through JM(I) values of YDH should be
started on a new card. This means that
the JM(1) coefficients Y(1,n) are read
in, then the JM(2) YDH(2,n) coefficients,
etc.

CARD 7

NAME: DE, TE

FORMAT: 2D15.8

DE is the dissociation energy and TE is
the electronic term energy of the electronic
state. Both are expressed in reciprocal
centimeters. DE is the difference between
the minimum in the potential of the electronic
state and the dissociation energy. TE is

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the energy separation between the minimum
of the potential curve and the minimum
potential on the ground state of the mole-
cule. If the ground state is being
investigated, TE is omitted.

CARD 8

NAME: VFIN, VINC

FORMAT: 2F6.2

VFIN is the largest vibrational quantum
number, v, for which the RKR routine
calculates the classical turning points
r minimum (RMIN) and r maximum (RMAX).
The turning points are calculated starting
with value of $v = -0.25$ and for each value
of v from 0 to VFIN in increments of
VINC. It is not necessary that either
VINC or VFIN be whole numbers. That is,
both may be decimal fractions. The quantity
VFIN/VINC must not exceed 398.

CARD 9

NAME: IOPG

FORMAT: I1

IOPFG is the Klein action integral. "I"
(see Eqs (32) and (81)), print switch.

All iterations are printed if IOPFG=1.

If IOPFG=0, these values are not printed.

CARD 10

NAME: RLIM1, RLIM2, NEXT

FORMAT: 2F6.2,I2

FLIM1 and FLIM2 are the inner and outer
limits of r, respectively to which the
RKR curve will be extended. The curves
will be extended by fitting formulas to
points making the inner and outer portions
of the curves plus any extra radius-
potential energy pairs input as data to
guide this fit. FLIM1 and RLIM2 also
determine the range over which the final
IPA curve will be expressed. RLIM1 and
RLIM2 should be sized to contain any
inner and outer radii generated by the
RKR and IPA programs.

NEXT is the number of extra data points
which will be used to guide the extension
of the curve. NEXT must be less than 25
and may be 0 if no extra data points are
to be added.

These data points must be obtained in one
manner or another. The program does not

specify how. But if these points are
available, this card makes provision for
entering them into the program.

CARDSET 11

NAME: Rl(I),PEl(I), where I = 1 to NEXT

FORMAT: (4X,1PD16.9,7X,D16.9/)

If NEXT = 0, these cards are omitted.

Rl(I) and PEl(I) are the radius and
potential energy pairs which will be used
to guide the extension of the RKR curve
which will be adjusted by the IPA program.
Rl(I) should be in angstroms. PEl(I)
should be in reciprocal centimeters.
These NEXT points, along with a given
number of points from the inner and outer
ends of the RKR curve, will be used to
obtain a fit to formulas as described
below to extend the original RKR curve to
the RLIM1 and RLIM2 limits.

CARD 12

NAME: KFIT(1),KFIT(2),KOUT(1),KOUT(2),
             KOUT(3),KOUT(4)

FORMAT: 6I5

KFIT(1) is the number of constants (An)
used in fitting a formula to the inner

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portion of the RKR curves. The formula is of the form:

$$V(r) = 10^{A1+A2*X+A3*X^2}\dots \tag{136}$$

where

$$x = \frac{r_e - r}{r_e}$$

KFIT(1)+2 is the number of data points taken from the inner portion of the RKR potential. These points, along with any extension data contained in CARDSET 11 for the inner portion of the curve, will be used to guide the extension of the curve to RLIM1. KFIT(2) is the number of constants (terms) used in the formula to extend the outer portion of the curve to RLIM2. The formula is of the form:

$$V(r) = A1\left(\frac{1}{r}\right)^{KOUT(1)} + A2\left(\frac{1}{r}\right)^{KOUT(2)} + A3\left(\frac{1}{r}\right)^{KOUT(3)}$$

$$+ \dots \tag{137}$$

KOUT(I), as shown above, is the power to which each 1/r term is raised. KFIT(2)+4 of the outermost turning points of the original RKR potential plus any

outer turning points included in CARDSET

11 are used in extending the curve to

RLIIM2.

If CARD 12 is blank the default values for

KFIT(1) through KOUT(4) are "2,4,0,6,8,

and 10" respectively.

CARD 13

NAME: IPNRKR,IPNIPA

FORMAT: 2I2

These two values in Vidal's original program

controlled the punching of an output deck

for the RKR and IPA programs. As the

PUNCH statements have been changed to

comment cards, these two inputs should be

0 until the program in the appendix is

modified. In the original program, if

IPNRKR and IPNIPA equaled 1, the card

decks were punched.

CARD 14

NAME: LTEST

FORMAT: I1

If LTEST = 0, the IPA routine is skipped

and the program proceeds to read in the

next set of data starting with the quantity

ITEST. See CARD 1.

This completes the input required to run the RKR portion of the program. Input required for the IPA portion of the program will be presented with the discussion of the IPA calculations.

The following section discusses the functions of each of the major routines of the RKR program in the order which they are used. The headings used are the titles of the subroutines. Sections of the program which have a physical significance and are helpful in understanding the flow of the program are highlighted. Numerical techniques which perform the RKR calculations are discussed in more detail to aid the reader in understanding the technique. Calculations which are straightforward and not necessary to understanding the program are not described.

The line numbers in parenthesis refer to lines in the program in this appendix. In this development, program symbols corresponding to the mathematical symbols defined for the RKR calculation are given immediately following the mathematical symbols to which they correspond. The symbols are placed in brackets.

PROGRAM MAIN

PROGRAM MAIN acts as a controller directing the major objectives of the whole program, the calculation of an RKR curve and its adjustment by the IPA routine.

MAIN starts by insuring that mass units of the atoms are expressed in terms of the Carbon-12 system making conversions as directed by input data in IIMS (lines 12,23,24,28). The reduced mass, ZMU, is calculated in AMU's (line 27).

The Dunham constants, YDH, as specified by CARDSET 6, are read as a result of the statement CALL YDHP11 (line 30). The Dunham constant Y_{01} is assigned to "BE" the normal name of that spectroscopic constant as shown in Table I (line 31). Then using BE, the internuclear equilibrium distance, r_e, is calculated in angstroms according to the following formula:

$$ r_e = \frac{FAC}{(BE)^{\frac{1}{2}}} = \left(\frac{h\ N_A}{4\pi c\mu Be} \right) \times 10^8 \tag{138} $$

Then Y_{00} is calculated according to Eq (6) (lines 35 and 36).

SUBROUTINE RKR

This routine is called from line 70 of PROGRAM MAIN.

First a calculation is performed to determine the number of $G(v)$ energy levels which will be evaluated in the RKR routine. This number is assigned to the variable "M" (lines 34-39). Then values of the vibrational quantum number, v, for the $G(v)$ energy levels are calculated (lines 44 and 45). In the program, the term "TEMP" corresponds to "v" and the term "U" to $G(V)$. The function POLY performs

the calculation of U [Gv] according to Eq (87) (line 46, statement label 110).

The program calculates, by an iterative technique, the value of "v_0" corresponding to Eq (90) (lines 51-62). It uses the Newton-Raphson method to find the value of "v_0" at which $Gv+Y=0$ (Eq 89)). The program uses "$v^* = Y_{00}/Y_{10}$" as its first estimate of "v_0" (line 55). From Eq (90), it can be determined that "v_0^*" is approximately "1/2" quantum units larger than the true value. Next, the value "$G(v_0^*)+Y_{00}$" is calculated (line 56). The Newton-Raphson method is used to converge to the value of "v_0" which satisfies "$G(v_0)+Y_{00}=0$" (lines 57-62, between statement labels 120 and 130).

For illustrative purposes, the Newton-Raphson method may be formulated as:

$$x_2 = x_1 - \frac{f(x_1)}{f'(x_1)} \qquad (139)$$

By the definition of $f'(x)$:

$$f'(x) = \frac{f(x_1)-f(x_2)}{x_1-x_2} \qquad (140)$$

Hence:

$$x_2 = x_1 - f(x_1) \left[\frac{x_1 - x_2}{f(x_1) - f(x_2)} \right] \qquad (141)$$

which corresponds directly to format of line 58. In Eq (141) $f(x)$ corresponds to "$G(v_0)+Y_{00}$". Loop 120 is repeated until a value of "v_0" is obtained such that "$G(v_0)+Y_{00}$" is close to 0 (line 57, statement label 120).

The remaining portion of the RKR routine, from statement label 130 to the end of the program, performs the integration required to solve Eqs (88) and (93) for "f" and "g". These, in turn, provide the classical turning points RMIN and RMAX of Eq (94). RMIN and RMAX values are obtained for each value of "v" [TEMP(I)] and corresponding "G(v)" [U(I)] as selected by inputs VFIN and VINC.

The solutions of the integrals for "f" and "g" contain a singularity. When "G(v´) = G(v)", the denominator [DENQ] of Eqs (88) and (93) go to 0 (lines 82,83,102, and 110). This singularity handled by assigning an "artificial" upper limit "v" [BS] to the integrals which is smaller than the true upper limit of the integral, TEMP(I), for the energy level "G(v)" [U(I)] involved. The artificial upper limit, BS, is allowed to approach the true value of "v" [TEMP(I)] in increasingly smaller steps until the solution of the integrals for two consecutive values of BS meet certain criteria. As BS is changed, the dv [d(BS)] contribution to the integrals is calculated and added to the sum for the integrals of "f" and "g". The rate at which BS approaches TEMP(I) is calculated in lines 72 and 130.

The criteria used for determining whether the solutions to the integrals are close enough to their true solution are given in lines 120-124 (statement labels 250-260). FEG is the value of the integral "f" for a given value of BS_n (line 120). FEG2 is the value by which the integral for

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"f" is in increased for the new value of BS_{n+} . Thus, if the ratio of the change in the value of the integral (FEG2) to the previous value for the integral (FEG) is less than 0.5×10^{-7} , the accuracy to which "f" has been determined is considered to be satisfactory. GEG2 and GEG in line 121 are tested in the same manner. In line 122, a ratio of changes (FEG2/FEG1) in the value of the integral "f" (FEG) for two consecutive calculations greater than 0.9 indicates that the accuracy of the integration is reaching a limit and should be halted. First, a ratio greater than 0.9 could indicate that the convergence to the true value is slower than desirable. Second, stopping the integration at this point is justified if the FEG1, FEG2 values are small. It is assumed that they are small. Similar arguments are given for GEG2 and GEG1.

The RKR program contains two integration routines. For the first three adjustments of BS, the upper limit of integration for "f" and "g", a Simpson rule integration is used. Lines 77-92 perform the integration of the functions for "f" and "g" over a range from VMIN (v) to BS on the first cycle. On the second cycle, VMIN is equated to BS, the lower limit of integration and a new upper limit BS is established as previously explained. In line 77-92, UV corresponds first to the v' and then to the $(G(v)-G(v'))$ of Eqs (88) and (93). And, expressed in the notation of the computer program, EV is the $G(v')$ and BI is the $B(v')$ of Eqs (88) and (93).

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For the fourth through the twentieth adjustments of BS, a Gaussian integration routine is used to provide a higher degree of accuracy. The routine is contained in lines 93-113 (from statement label 180 through label 240). The abscissas [XGAUS] and weight factors [AGAUS] are listed at the start of the RKR routine for a Gaussian integration of moments where K=0 and N=4,6, or 8 depending upon the success of the iteration. The formula for the integration is (Ref 1:931):

$$\int x^k \, f(x) \, dx \approx \sum_{i=1}^{n} w_i \, f(x_i) \qquad (142)$$

Where

x_i = abscissas

w_i = weight factors

Finally, RMIN and RMAX for each v , [TEMP] and Gv , [U], are calculated in lines 139 and 140 per formula (95).

After all turning points have been calculated, control is transferred back to the program MAIN where CALL YDHP11(0) causes the input Dunham coefficients plus Y_{00} to be printed.

Routines EXTEND, GLSQ, FUNC, and EXTEND

The subroutine EXTEND, in conjunction with the above routines, performs a least-squares fit to the inner and outer portions of the RKR and extend them to RLIM1 and RLIM2 respectively. The fits are performed according to Eqs (117) and (118). Eq (117) expressed in the notation used in lines 16-31 of GLSQ and 31-39 of FUNC becomes:

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$$\text{Log}_{10}U(I) = Z(I) = B1[x(1)]^0 + B2[X(I)]^1 + B3[X(I)]^2 + \dots \quad (143)$$

$Z(1)$ is calculated in EXTEND and, as expressed, is the log to base ten of the energy. The inner turning radii, RMIN, are transferred into the $X(I)$ array, and then the function FUNC (called from line 18 of GLSQ) transforms the variable X to the form given in Eq (117), i.e.,:

$$X = \frac{r_e - r_{min}}{r_e} \quad (144)$$

Expressing Eq (124) in the notation of GLSQ yields a matrix equation of the form:

$$\begin{bmatrix} n & \Sigma x_i & \Sigma x_i^2 & \Sigma x_i^3 \\ \Sigma x_i & \Sigma x_i^2 & \Sigma x_i^3 & \Sigma x_i^4 \\ \vdots & & \vdots & \\ \Sigma x_i^3 & & \Sigma x_i^6 & \end{bmatrix} \begin{matrix} B \\ B \\ \vdots \\ B \end{matrix} = \begin{matrix} Z \\ Z \\ \vdots \\ Z \end{matrix} \quad (145)$$

or

$$A(J,K) * B(J) = BB(J)$$

where $A(J,K)$ is formed in line 22 of GLSQ. $BB(J)$ is formed in line 20. In line 23, the routine MATINV solves Eq (126) by inverting $A(I,J)$, multiplying it times $BB(J)$ and returns the B vector in place of the BB vector. The operation performed by MATINV may be expressed as follows:

$$B(J) = A(J,K)^{-1} BB(J) \quad (146)$$

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A similar pattern is followed for the outer portion
of the curve except that formula (118) is used instead of
(117).

After the fits have been performed, EXTEND calculates
20 additional points between the inner limit of the RKR
curve and RLIM1, and 99 additional points between the outer
end of the RKR curve and RLIM2. The points are calculated
using fitting Eqs (117) and (118).

The change made in line 37 of FUNC affects the manner
in which the curve fit is performed for values of r between
the inner limit of the RKR curve and RLIM2. The difference
occurs only if the extension data input in CARDSET 11 has an
r , [R1(I)], between RLIM1 and the inner limit of the RKR
curve. When FUNC is called from GLSQ which, in turn, has
been called from EXTEND with an argument of "1" (CALL GLSQ(1)),
the inner turning points are to be fit according to Eq (117).
As written in Vidal's original program, line 37, "IF (XX.GT.AAA)
RETURN", permitted the routine to continue on to the next
statement when extra extension data was added with a radius
less than the inner limit of the RKR curve [RAA]. This
resulted in the returning of the energy [U(i)] of Eq (143)
instead of the log of the energy, [Z(I)]. Then when the energy
and the log of the energies are mixed in the fitting process,
the fit is incorrect. By changing line 37 to "IF(KK.EQ.1)
RETURN", the fit for the inner turning points is performed
correctly. The variable "KK" is always "1" when the fit to

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the inner portion of the RKR curve is performed (line 31 of

EXTEND). This change does not affect the operation of the

program when FUNC is called from other routines. When FUNC

is called from line 56 of FIPA, "KK" is equal to "0".

Hence, the radius [XX] is the controlling factor in lines 7

and 8 of FUNC. Then when the potential energy for the exten-

sion points are being calculated, the routine proceeds through

line 37 as it should.

This concludes the discussion of the RKR calculations.

Subroutine FIPA

Control of the program is transferred from MAIN to

FIPA by line 83. This routine controls the IPA portion of

the program. In the following section, the inputs required

to run the FIPA routine are described.

FIPA Input

CARD 14

NAME: LTEST

FORMAT: I1

This input description is repeated from

the RKR section. If LTEST is not equal

to "0", the IPA calculation is continued

and an IPA data deck is required as

described below.

CARD 15

NAME: NI,NS,IPSIQ,MAXITT,EPSC

FORMAT: 4I4,D10.0

If NI=1, data from each SCHR iteration is printed.

If NI=0, the iterations are not printed.

If NS=1, the wavenumbers are printed at every IPSIQ points.

If NS=0, the wavenumbers are not printed.

EPSC is the convergence criterion for the solution of the Schroedinger wave equation for its energy eigenvalues, E_{vJ} . An EPSC of 0.001 wavenumbers is suggested as a good starting value.

MAXITT is the maximum number of times SCHR will attempt to satisfy the convergence criterion.

CARD 16

NAME: RMIN, RMAX, M NRPTT, NPL, MCH, LSW

FORMAT: 2F10.0,5I5

RMIN and RMAX are the minimum and maximum values over which the potential is evaluated by the IPA procedure. M is the number of points at which the potential will be evaluated. The maximum M should be 2401, for the program as written in the appendix.

Memory size limitations may dictate that
fewer points be calculated.

NRPTT is the number of iterations performed
in the IPA routine. On the last iteration,
the rotationless potentials are calculated
to obtain G_V and B_V .

NPL is the number of terms in the Legendre
polynomial used to represent the correction,
ΔV , to the energy potential.

MCH is the control used to punch a deck of
the G_V and B_V values. As stated, all
PUNCH cards have been changed to comment
cards. If PUNCH statements are reactivated
and MCH=1, the decks will be punched. Note
that PUNCH is not a legitimate Fortran V
statement.

If LSW=0, the first and last iterations of
the IPA program are printed.

If LSW=1, all iterations are printed.

CARDSET 17

NAME: (MTRMIN(I),MTRIAL(I),BJTT(I),I=1,11)

FORMAT: (6(I2,I3,F7.0)/5(I2,I3,F7.0))

MTRMIN and MTRIAL defines the range of
vibrational quantum numbers, v , which are
investigated in the Schroedinger calculations.

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These variables are input as "v+1" values. Hence, an input of "1" corresponds to the vibrational quantum number "0", etc. BJTT determines the "J(J+1)" values for which the corresponding MTRMIN-MTRIAL range is calculated. The number of BJTT values is limited to 11. The last BJTT value must be "0" so that the rotationless potentials may be calculated.

This completes the input required for the RKR-IPA program.

The IPA routine uses the Numerov-Cooley method to find numerical solutions to the Schroedinger equation (Refs 11:363; 14:1872). The routine presented here provides a method for finding solutions for bound states. Vidal also mentions methods for solving unbound states (Ref 43:7). They will not be presented here.

Terms initialized at the start of FIPA are described here. AZERO is the Bohr radius as measured in angstroms. Lines 47-49 repeat the calculation of "r_e", [RRE], the internuclear equilibrium separation according to Eq (119). Line 50 converts "r_e" [CRE] from angstroms to units of Bohr Radii.

Lines 51 and 52 insure that the limits of the extended RKR curve are beyond the RMIN-RMAX limits specified by the IPA input CARD 16. If not, the RMIN-RMAX limits are redefined to conform to the limits of the extended RKR curve.

Line 53 defines the step size of r [RH] for which the potential curve is calculated.

DO-loop 140 calculates the radius-potential energy pairs [P(J) and V(J)] which will be used in the IPA routine. The line of statement label 140 calls on the function FUNC to generate potential energies for each value of r . FUNC obtains the potential energies, V(r), for each value of r by performing a Lagrangian interpolation on the radius poten- tial-energy pairs of the extended RKR curve. The Lagrangian technique may be expressed as follows (Ref 16):

$$V(r) = \sum_{i=0}^{n} \prod_{j=0}^{n} \frac{r-r_j}{r_i-r_j} \qquad (147)$$

where r is the value for which V(r) is to be calculated. In FUNC, four points on both sides of r are used for the interpolation of each point. In this manner, the V(r) values are obtained for evenly spaced values of r from the unevenly spaced potentials of the RKR routine.

The section of FIPA following the comment "SEARCH FOR CENTRIFUGAL BARRIER," finds the maximum energy which a mole- cular system can have for a given rotational energy level, J , for a bound state. Expressed in the notation of the computer program, the effective potential energy, SX, is calculated by the formula:

$$SX = V(I) + ABE* \left[\frac{RE}{P(I)} \right]^2 *AJTT \qquad\qquad (148)$$

In lines 65-72, SX is calculated for rotationless potential
energy and radius pairs, [V(I) and P(I)]. Hence, SX is
the effective potential energy for a given radius and rota-
tional quantum level, J . Fig B-1 shows the behavior of
the potential for increasing J values.

The program first finds the minimum of the potential
curve and assigns it to ASX. Once the minimum has been found,
the potential increases with r . Each successive larger
value of SX is assigned to TX. At the same time, ASX is
equated to SX. This process is continued until the effective
potential energy curves reaches a maximum as in Fig B-1.
This maximum value of SX is retained in TX and is the sought
for centrifugal barrier.

Having found the largest permissible value of SX (TX)
for a given J value, the routine BETRL (line 73 of FIPA)
finds the E_{vJ} [ETRIAL] which is just smaller than the centri-
fugal barrier, TX, and the corresponding rotational quantum
number plus one (v+1). The "v+1" value is returned as NTRIAL
to the FIPA routine. NTRIAL is then compared with input
MTRIAL(KI) and the smaller value retained in the variable
MTRIAL(KI) (lines 74-76). The ETRIAL corresponding to the
retained MTRIAL(KI) is stored in the array variable ER(KI)
(line 77).

V(r)

Centrifugal
Barriers

J_2

J_1

$J=0$
0

Internuclear Separation
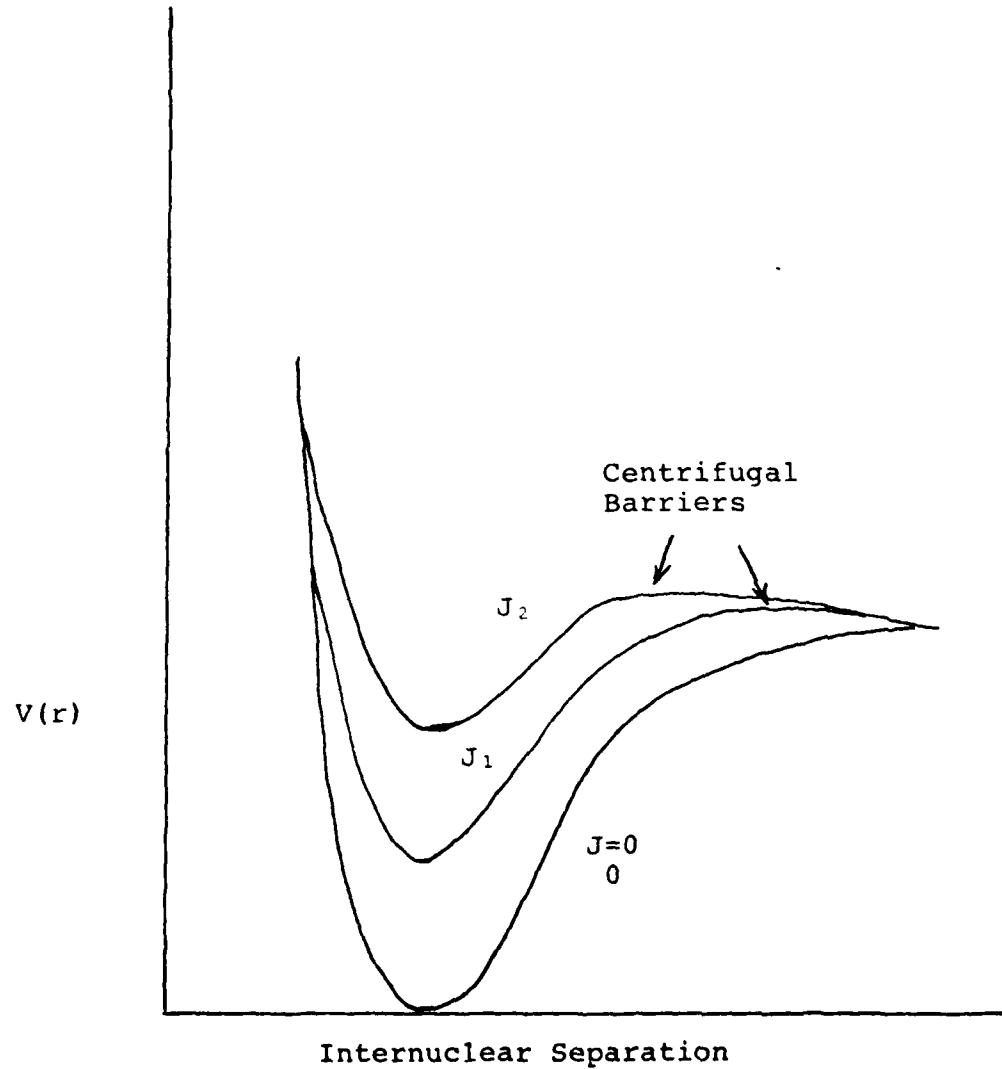
Fig B-1.　　Effective Potential Energy Curves for
Three Rotational Energy Levels,
J_1, J_2, and J_0

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In addition to calculating the effective potential energy, the routine BETRL also calculates the values for B_v [BTRIAL], where J does not equal 0. The variable B_v is determined according to the following relationship:

$$B_v\big|_J = \frac{\partial E_{vJ}}{\partial J(J+1)} = \frac{\partial ETRIAL}{\partial J(J+1)} \qquad (149)$$

The next step is to determine the range of internuclear separations, r, which is to be considered in the IPA routine. This range is predetermined by the MTRIAL(J) and BJTT(J) values. This range is assigned to the variables RMII and RMAA.

DO-loop 200 performs the first step in identifying the RMII and RMAA values. The third line of the loop finds the first energy level, V(I), on the inner portion of the RKR curve which is smaller than or equal to the ER(KI) value being investigated. The value of the subscript for that V(I) is retained in N3AA. Line 88 finds the first energy level, V(I), on the outer portion of the RKR curve which is just larger or equal to the ER(KI) value being investigated. The subscript of that V(I) is retained in N3BB. The process is repeated for each ER(KI), and the smallest value of N3AA is retained as N3A (line 92, statement label 220). The largest value of N3BB is retained as N3B. The values N3A and N3B are the subscripts of the array P(I) which provide:

$$RMII = P(N3A) \qquad (150)$$

$$RMAA = P(N3B) \qquad (151)$$

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In this manner, the limits of r over which the IPA routine
and Schroedinger equation are to be investigated have been
established so that they are consistent with the specified
values BJTT(I) and MTRIAL(I) and the centrifugal barrier.
The values MTRMIN(KI) along with the MTRIAL(KI) values which
have been adjusted to be consistent with the centrifugal
barrier, determine the range of vibrational quantum numbers,
v , over which the RKR curve is evaluated for each value of
BJTT(KI). This is true for all iterations of the IPA routine
except the last iteration.

The range of vibrational quantum numbers, v , which
are considered in the last iteration for each BJTT(KI) value
may be different from that range specified by NTRMIN(KI) and
MTRIAL(KI). The investigation of potential energy ranges
specified by RMII and RMAA may uniquely define energy levels,
E_{vJ} , for a specific BJTT(KI) value not included in the input
NTRMIN(KI)-MTRIAL(KI) values. For the last IPA iteration,
MTRIAL(KI) is replaced by LTRIAL(KI).

If the radius of the centrifugal barrier is greater
than RMAA and, thus, outside the region investigated by pre-
vious iterations of the IPA routine, the maximum energy
level to be investigated for a given value of BJTT is the
smaller of the two following values:

$$TX = V(N3B) + ABE(RRE/RMAA) *AJTT \quad \text{(line 99)} \qquad (152)$$

$$SX = V(N3A) + ABE*(RRE/RMII) AJTT \quad \text{(line 101)} \qquad (153)$$

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where V(N3A) is the potential energy corresponding to RMAA, and V(N3A) is the energy corresponding to RMII.

If the radius of the centrifugal barrier is smaller than RMAA, then the energy of the centrifugal barrier, YMAX(KI), for a given BJTT(KI) is compared with the value in Eq (152) and the smaller value retained for investigation and assigned to the variable. BETRL(TX) then identifies the first quantum vibrational-rotational energy level below TX for a given BJTT(KI). Then "v+1" is assigned to the LTRIAL(KI) variable.

Subroutine PLEGEN

Subroutine PLEGEN and lines 109-119 perform the calculations necessary to give a numerical value to the function f(r) which will be used to perform the calculations of Eqs (113), (114) and (115).

First, all the radii measurements are converted to units of Bohr radii.

Kosman and Hinze chose Legendre polynomials $P_i(x)$ to represent the $f_i(r)$ functions (Ref 23). Vidal found that attempting to extend calculations beyond RMII and RMAA, as specified by E_{vJ} , produced large oscillations. He finally settled upon a combination of Legendre polynomials and an exponential function to dampen the oscillations. This combination improved the convergence of the IPA method. The expression Vidal used is as follows (Ref 41:50):

$$\Delta V_0(r) = \sum_i c_i P_i(x) \exp(-x^{2n}) \tag{154}$$

where the typical range for "n" is $1 < n < 5$. The Gaussian part of Eq (154) provides a smooth cutoff avoiding unphysical oscillations. The Legendre polynomials are calculated using the standard recursion relations (Ref 6:424):

$$(n+1) P_{n+1}(x) = (2n+1) X P_n(x) - n P_{n-1}(x) \tag{155}$$

where $P_1 = 1$ and $P_2 = X$.

Kosman and Hinze used a linear relationship between r and X such that $X=1$ for $r=r_{max}$ and $X=-1$ for $r=r_{min}$. Vidal found this relationship to provide poor convergence when dealing with vibrational levels all the way to the dissociation limit and when dealing with anharmonic potentials. He stated that the reason for the poor convergence in the case of a highly anharmonic potential is that a linear interpolation tends to optimize only the outer turning points of the rotationless potential. To avoid this, Vidal chose a nonlinear interpolation given by:

$$X = \frac{(r-r_e)(r_{max}-r_{min})}{(r_{max}+r_{min})(r_e+r)-2r_{max}r_{min}-2r_e r} \tag{155'}$$

This relation assumes $X=1$, for $r=r_e$, and $X=0$, for $r=r_{max}$ and $X=1$, for $r=r_{min}$. The interpolation becomes linear for:

$$r_e = \frac{r_{max} + r_{min}}{2} \qquad\qquad (155)$$

This formulation treats the inner and outer turning points with comparable weight and reduces the number of Legendre polynomials in Eq (154).

Using these formulas, PLEGEN and DO-loop 270 calculate a Legendre polynomial $F(J,I)$ with "NPL" terms (i.e., J=1 to NPL) for each of the turning points $P(I)$ on the RKR potential where I=1 to M .

The section of FIPA from statement label 180 through the second line after statement label 780, contains the statements necessary to solve the Schroedinger wave equation (SWE) for its eigenvalues, E^0_{vJ} , and radial wave functions, ψ^0_{vJ} . It also calculates the correction to the potential, $\Delta v_0(r)$, necessary to make the eigenvalues obtained from the SWE consistent with those observed experimentally. The program returns to statement label 180 until all the "NRPTT" iterations have been completed. On the last iteration (NREP=NRPTT), lines 123-125 specify that NT3=NT1. The term "NTT" is equal to the number of BJTT values which are greater than "0".

As noted, the first use of the perturbation technique to adjust approximate potential energy curves is attributed to Hinze and Kosman (Ref 23). The technique used in this program to solve the Schroedinger equation is the Numerov-Cooley method (Refs 11; 14). The Numerov-Cooley method of

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solving the SWE was used by J. K. Cashion to test the validity
of approximate eigenvalue equations developed by Pekeris for
a rotating Morse oscillator (Ref 11).

The routine presented in this paper solves the SWE
for bound states. Vidal discusses techniques for handling
quasibound states. The techniques for evaluating quasibound
states are not part of the present program but are here
briefly discussed. One approach, Vidal used for quasibound
states involved starting the integration of the SWE at small
internuclear distances and looking for the maximum of the
internal amplitude inside the centrifugal barrier as well as
the phase shift of the partial wave outside the centrifugal
barrier using a Breit-Wigner parametrization (Ref 12). Vidal
also used a second approach in the same work (Ref 43). For
quasibound states, he introduced an artificial barrier at
large internuclear distances permitting the use of the
Numerov-Cooley method. The eigenvalues he found in this manner
were slightly higher than the energy eigenvalues derived
from the maximum of the internal amplitude. Proper choice
of the barrier kept the differences within the standard
errors of the measurement. Using this technique, Vidal stated
the same numerical method can be used for both quasibound and
bound states.

Continuing with the program, as presented in this
paper, it is necessary to transform the energy used in the
SWE to units which are consistent with the units of length

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being used, Bohr radii. Thus far, energy has been expressed
in terms of inverse centimeters, wavenumbers. To convert
wavenumbers to energy units consistent with Bohr radii, it
is necessary to divide by this factor (Ref 11:1873).

$$\frac{\hbar N_A}{4\pi c a_0 \mu_A} = \frac{60.19972628}{\mu_A} \quad \text{wavenumbers} \qquad (156)$$

where $a = 0.52197706$ and N_A = Avogadro's number. The inverse
of this quantity is assigned to the variable ZEIN.

The effective potential energies (given according to
Eq (148)) for the first BJTT value, for the whole range of
the RKR curve, is calculated in DO-loop 340. The energy
reference frame is shifted so that the dissociation energy
[DE] is the zero energy level.

The lines between statement labels 340 and 360,
establish the values of $J(J+1)$ [BJTT(KI)] and the range of
vibrational quantum numbers, NTRMIN through NTRIAL which
will be considered for the experimental energy eigenvalue
V(I) of statement label 340. Loop 660 also starts here.

If it is the last iteration of the IPA routine
(NREP=NRPTT), the range of vibrational quantum numbers
starts at "v+1=1" and extends through LTRIAL(KI) for each
corresponding value of BJTT(KI). This range is specified by
lines 140 and 141.

The value of $J(J=1)$, to be investigated on a cycle
of loop 660, is assigned to the variable AJTT in statement
label 360.

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CALL BETRL(TX) this time calculates all the term values, E_{vJ} [ETRIAL], for all values of "v+1" from 1 to NTRIAL with J specified by $J(J+1)$ [AJTT]. B_v [BTRIAL] is also calculated over the same range. The rotational quantum number J corresponding to $J(J+1)$ is assigned to the variable LJT in line 142.

The Schroedinger loop which calculates the radial wave functions [P(J)], B_{vJ} [BCALC], and E_{vJ}^0 [ECALC] starts with line 152. The SWE loop (loop 600) starts by specifying the "v+1" values will be investigated, MTRMIN through MTRIAL. These variables were assigned their values in lines 137-141. Variables MA and MB are initiated to zero prior to entering the SWE routine.

Integer Function SCHR

The SCHR routine solves the Schroedinger equation by the Numerov-Cooley method. The routine is called by line 158 of FIPA. Using this method, each of the experimental term values is adjusted to be consistent with the whole RKR curve. Hence, all term values which were used to produce the RKR curve are indirectly used to adjust each eigenvalue, E_{vJ}, solution found by the SCHR routine.

Numerov-Cooley Method for Solving the SWE

The Numerov-Cooley method for solving the SWE is outlined here. Using Cooley's notation, the SWE may be expressed as follows:

$$P^2(r) = [U(R)-E]P(R) \qquad (157)$$

$$P^{(n)} = \frac{d^n P}{d R^n}$$

where $P(R)$ is the radial wavefunction and E are the eigen-
values of the SWE. Cooley defines the potential energy $U(R)$:

$$U(R) = [J(J+1)-\Lambda^2]R^{-2}-Z_aZ_bR^{-1}+E_{e1}(R) \qquad (158)$$

In this paper, the contribution of the Λ quantum number,
the z-component, due to the electronic angular momentum, is
ignored. The electrostatic Coloumb repulsion energy of the
nuclei, $Z_aZ_bR^{-1}$, and the electronic energy, $E_{e1}(R)$, make
up the vibrational $(v+1/2)$ term of the E_{vJ}'s as expressed by
Eq (2). The boundary conditions used are:

$$P(0) = 0, \text{ and } P(R) \text{ bounded} \qquad (158')$$

The following definitions are used to convert Eq (157)
to a finite difference equation:

$$R_i = h \qquad i = 0,1,2...n+1$$
$$P_i = P(R_i) \qquad (159)$$
$$U_i = U(R_i)$$

By dropping fourth order and higher terms in the series:

$$P_{i+1} + P_{i-1} = \sum_{k=0}^{\infty} \frac{2h^{2k}}{(2k)} P_i^{2k} \qquad (160)$$

and by using the different equation to replace P_i^2, Cooley
obtained the integration formula:

$$P_{i+1} + P_{i-1} - 2P_i = h^2(U_i - E)P_i \qquad (161)$$

The error involved in Eq (161) is approximately $\frac{h^4}{12} P_i^{(4)}$.
He then presented a higher order integration formula, developed
by Numerov, which does not involve the calculation of
additional P_i's. The formula is obtained by subtracting
the product of $\frac{h^2}{12}$ times the following series:

$$P_{i+1}^{(2)} + P_{i-1}^{(2)} = \sum_{k=0}^{\infty} \frac{2h}{(2k)} P_1^{(2k+2)} \qquad (162)$$

from Eq (160). Then dropping sixth and higher order terms
in h , gives the differencing scheme used in Vidal's program:

$$Y_{i+1} + Y_{i-1} - 2Y_i = h^2(U_i - E)P_i \qquad (163)$$

where:

$$Y_i = P_i - (h^2/12) P_1^{(2)} = [1-(h^2/12)(U_i-E)] P_i \qquad (164)$$

The error for this formula is approximately $-\frac{h^6}{240} P_i^{(6)}$.

For all unbound states, $E>U(\infty)$, solutions exist for
all E and, according to Cooley, may be approximated by using
Eqs (161) or (163) to integrate outward starting with
boundary values:

$$P = 0 \ , \ P = \text{a small arbitrary number} \qquad (165)$$

For bound states, $E<U(\infty)$, only discrete eigenvalues,
E , exist. The boundary conditions for solution to Eq (163)
are:

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$$P(0) = 0 \tag{166}$$

and for $P(R)$ bounded:

$$P_{n+1} = \text{a small arbitrary number} \tag{167}$$

$$P_n = P_{n+1} \exp\left(R_{n+1}\sqrt{U_{n+1} - E} - R_n\sqrt{U_n - E}\right) \tag{167'}$$

The second condition results from the assumption that at R_n , $U(R)$ is slowly approaching a constant value.

The method of solution involves starting with some E (i.e., the experimentally obtained term values) and with the boundary conditions specified by Eq (166) integrate outward to some point R_M using Eq (163). Then the wavefunctions P_i to P_m are normalized to P_m:

$$P_i^{out} = P_i/P_m \qquad i = 1,2,3,\ldots m \tag{168}$$

Then the same procedure is followed starting at P_{n+1} and integrating inward to P_m . Again, the P_i values are normalized, this time, using the P_m^{in} value obtained in the inward integration. Hence, $P_m^{out} = P_m^{in} = 1$. At this point, a correction for E is determined from the difference in slopes of the two portions of the curve ($R < R_m$ and $R > R_m$). The inward-outward, E correction cycle is repeated until the value for E on successive iterations differs by some established limit, ε [EPS]. When this occurs, a satisfactory eigenvalue E has been obtained.

The correction formula is expressed as follows:

$$D(E) = (P'_{out} - P'_{in}) / \int_0^\infty [P(R)] \, dR \qquad (169)$$

where the P' terms are derivatives of the wavefunctions at R_m resulting from the inward and outward integration. Expressed as a difference equation which is consistent with Eq (163) $D(E)$ is:

$$D(E) = [(-Y_{m-1} + 2Y_m - Y_{m+1})h^{-2} + (U_m - E)P_m] / \sum_{i=1}^n P_i^2 \qquad (170)$$

Convergence difficulties with this approach may be encountered. Cooley describes the convergence of the technique and how to recognize what types of difficulties can be encountered. These will not be covered here.

Problems with convergence will be encountered if a $P(R)$ is selected so that the magnitude of radial wavefunction at R_m is "0". Recalling that the procedure calls for normalizing the radial wavefunction $P(R)$ at the point P_m, it is clear that dividing by a number close to "0" into larger numbers can introduce significant errors.

Cooley's program used the Numerov method to solve the SWE. His program was structured so that $D(E)$ must be decreasing in magnitude from one iteration to the next; then, the $D(E) < \varepsilon$ convergence criterion is applied.

The problem of stopping at a radius R_m when $P_m(R)$ is zero, is handled rather nicely from the knowledge that for

the anharmonic motion of a diatomic molecule, the wavefunc-
tion P(R) reaches a maximum at a radius near the outer por-
tion of the potential. Thus, Cooley started his inward integra-
tion and stopped at the value of R_m such that P_m had stopped
increasing, i.e., it had reached its maximum. This method
finds the largest P and, hence, keeps the correction
technique from becoming accidentally unstable due to a poor
choice of P_m. This value of R_m is retained and the outward
integration is then performed. This concludes the discussion
of Cooley's article. His article includes a derivation of
D(E) and further discussion of the convergence of the method.

The discussion of the SCHR routine is now continued.
As in previous sections, the notation in Vidal's program will
be placed in brackets following the notation of Cooley when
use of both is desirable.

The routine SCHR starts by initializing the values
H [H], h^2 [H2], and $h^2/12$ [HV] of difference Eqs (159), (163)
and (164). The value "NN" corresponds to the "M" of input
CARD 16. Line 13 sets E_{vJ} [E] equal to the value of ETRIAL(I)
where "I" corresponds to a "V+1" vibrational quantum number.
The "I" value is specified by FIPA, DO-loop 600.

The rotational quantum number J being considered
corresponds to the J(J+1) [AJTT] specified by statement
label 360 of FIPA. The E_{vJ} [ETRIAL(I)] was calculated by
CALL BETRL(TX), line 144 of FIPA.

Next, DO-loop 10 finds the value on the potential curve which is just greater than E_{vJ} [E] and identifies it temporarily by the subscript of V(LCRIT). If the inner potential V(IPP) does not extend above E_{vJ} [E], then an error message is printed indicating the failure of the integration routine with KERR=1. The loop 16 decreases the starting subscript of the potential to either V(1) or until "WCRIT>20.0" is satisfied. It is assumed that this criterion is sized so that for the minimum value of R considered, the magnitude of the wavefunction P(R) will be sufficiently small to satisfy the assumed boundary conditions, Eqs (166) and (167).

This assumption may be checked in the printout. Values for the inner and outer wavefunctions $P(R_{min})$ [S(MA)] and $P(R_{max})$ [S(MB)] are printed. In the introductory comments to his program, Vidal states that S(MA) and S(MB) should typically be of a magnitude of $1x10^{-10}$, if the RMIN and RMAX limits are wide enough. This implies that the "WCRIT>20.0" will produce S(MA) and S(MB) of similar magnitude.

The process is repeated to find the first value greater than E_{vJ} [E] at the outer end of the potential. The routine then extends the potential to sufficient magnitude of R so that the value of the outer wavefunction S(MB) will be sufficiently small. Again, an error message is printed with "KERR=2" if the outer portion of the potential does not extend above E_{vJ} [E].

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The values of NL1 and NL2 are assigned such that V(NL1) is the second value on the inner portion of the curve less than E_{vJ}[E] and V(NL2) is the first value greater than E_{vJ}[E] (lines 23 and 130). These values will be used as the limits S(NL1) and S(NL2) between which the number of codes (i.e., the number of times P(R) [S(R)] becomes zero) associated with each E are counted. This count is the determination of the vibrational quantum number v[KV] associated with that eigenvalue E_{vJ} (lines 120-123, DO-loop 70). These values are printed out in the program listing.

Following Cooley's method, the inward integration is started first. The outer numerical value for the wavefunction P_{n+1} [S(MB)] is assigned an arbitrary value of 1×10^{-10} (Eq (117)). The next point P_n [S(MB-1)] is evaluated according to Eq (167´).

The lines between statement labels 36 and 40 perform the inward integration until P(R) [S(I)] stops increasing. The largest value of the wavefunction, P_m, is assigned to the variable PM. The correspondence beween Eq (163) and the program is as follows:

$$Y_{i+1} + Y_{i-1} - 2Y_i = h^2 (U_i - E) P_i \qquad (163)$$

$$YA + YC - 2YB = H2*(GI)*S(M+1) \qquad \text{Line 66}$$

$$Y_i = [1 - h^2/12 (U_i - E)] P_i \qquad (164)$$

$$YC = [1.D\emptyset - HV*GI] (SM) \qquad \text{Line 68}$$

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The portion of the wavefunction obtained from the inward integration is normalized by PM_{in} .

If S(I) goes negative on the inward integration, an error message indicating the failure of the SCHR routing is printed with "KERR=3" indicating the source of the failure.

The process is repeated starting at the inner portion of the potential curve and integration continued out to the radius corresponding to the previously identified PM, the point at which the wavefunction first reached a maximum for the inward integration. This wavefunction from S(MA) to PM is normalized with PM_{out} . The variable DF corresponds to the denominator ΣP_i^2 of Eq (170) (statement label 53). The variable F corresponds to numerator and the correction to $E_{vJ}[E]$ is DE. This DE should not be confused with the DE of the rest of the program which is the dissociation energy.

The convergence criterion, as outlined by Cooley, is satisfied by the lines between statement labels 56 and 60. Restating that criterion, DE [DE=ABS($E_{new}-E_{old}$)] must be less than some ε [EPS] with the stipulation that E is converging on consecutive iterations. A converging E requires that DE be getting smaller and smaller. Vidal's program handles these requirements in the following manner. TEST is assigned a value of "-1". If the SCHR routine converges on every iteration, i.e., DE gets smaller on every iteration, TEST is assigned a positive value. Then line 112 is never applied. On the other hand, if DE increases, the

ε [EPS] criterion is never applied because TEST will remain

negative. Hence, DE must get smaller which results in TEST

being assigned a positive value before the convergence

criterion is checked. This prevents the routine from

accidentally satisfying the convergence criterion without true

convergence being obtained. This still does not prevent the

program from jumping from a solution for one vibrational

quantum number v to an eigenvalue associated with a

different v . This error can be detected in the printout

by observing that a proper ordering of v[KV] is not maintained.

DO-loop 70 counts the number of times the wavefunc-

tion P(R) [S(J)] becomes "0". This number, as noted,

corresponds to the vibrational quantum number v for eigen-

value E_{vJ}[E] .

The last computation is the normalization of the wave-

function P(R) [S(J)] so that

$$\int_{J=MA}^{MB} S(J) \star S(J)\, dH = 1 \qquad (171)$$

The remainder of the SCHR routine is concerned with the option

of printing the solution of the routine. This option is con-

trolled by the "NS" input of CARD 15.

FIPA (Continued)

At this point, control is returned to FIPA. If the

SCHR routine has been successful, a wavefunction ranging from

S(MA) to S(MB) is returned along with a new eigenvalue E_{vJ} [ECALC]. In this case, "SCHR=0" and the programs proceed to statement label 420.

When "SCHR=1", this indicates that the SCHR routine was converging towards the limit ε [DE], but that the limit was not achieved in the number of iterations permitted, MAXITT, specified by input CARD 15. In this case, the program proceeds to statement label 400, and LLK is incremented. The variable "LLK" is used to report the number of times the convergence criterion ε is not satisfied. This value is printed by the command in statement label 620.

If "SCHR=2" is returned from the routine SCHR, the routine has failed to converge for a specific E_{vJ} . The reason for the failure is specified by the value "KERR" specified in SCHR (lines 21, 37, or 69) and printed out by the command in statement label 83 of SCHR.

If SCHR fails, the program proceeds to statement label 300 and KLK is incremented. If the SCHR routine fails "KLIM" times (where KLIM is specified as "2" in line 147), the program is halted by CALL EXIT (line 163).

If SCHR has been successful at finding the wavefunction S(J) for a given eigenvalue ECALC, then control proceeds to label 420 where the limits of the Schroedinger loop are, if necessary, adjusted to be consistent with MA and MB. The expectation values of "$\left(\frac{1}{r}\right)^2$" are calculated for a specific

of v and J by lines 169 through 173.   Simpson's rule is
used to perform the required integration:

$$B_v = \frac{\hbar}{4\pi\mu c} \quad \left\langle \psi_{vJ} \left| \frac{1}{r^2} \right| \psi_{vJ} \right\rangle \tag{172}$$

where ψ_{vJ} is the numerical wavefunction S(MA) to S(MB)
returned from SCHR.

The eigenvalue ECALC is converted to the proper
units and the reference changed so the bottom of the potential
well is zero by adding the dissociation energy DE to the
potential (line 157).

The experimentally determined eigenvalue, ETRIAL(I),
(calculated from the Dunham coefficients by the routine PETRL),
is also returned to the reference frame where the bottom of the
potential well is zero (line 175).   The difference[DIFF]
between the experimental eigenvalue (ETRIAL) and the eigen-
value (ECALC) is then calculated.   The variable DIFF is the
ΔE_{vJ} of Eq (109).

Line 177 directs the program to advance to statement
label 540, if the program is in the last iteration of the IPA
routine as specified by NRPTT.   This skips several calculations
necessary to obtain the ΔV of Eq (113).   These are not
necessary because the last values calculated by the program
will be printed and the routines necessary to calculate
Eq (113) will be skipped.

If the program is not on the last iteration of the
IPA routine, it calculates (Eq (114)) the expectation values

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[FPL(k)] of the f(r)'s [FX(K,J)] of Eq (113) where the f(r)'s are expressed in terms of Legendre polynomials as expressed in Eqs (154), (155), and (155´). The polynomials for f(r) were calculated in DO-loop 270 FIPA (lines 180-186).

The reason for the statistical weight EWG in line 189 has not been determined at this time. It might be used to reflect the different uncertainties in the determination of ∇E_{vJ} for different positions on the potential curve.

Next I shall discuss the solving of Eq (115) for the coefficients c_i [COEFF(K)] . The equation is manipulated and constants calculated in the normal least-squares fashion according to Eqs (12-16).

The least-squares fit is performed according to the general formula:

$$B = (X^T X)^{-1} X^T \qquad (13)$$

where X^T corresponds to:

$$BL(K) = \sum_{k=1}^{NPL} DIFF \ast FPL(K) \qquad (172)$$

as defined by DO-loop 520. And $(X^T X)$ in notation of the computer program is:

$$AL(K,J) = \sum_{k=1}^{NPL} \sum_{j=1}^{NPL} FPL(j) \ast FPL(k) \qquad (173)$$

The errors associated with the calculations are tabulated in several ways. The sum of the errors, $\sum_{v} \Delta E_{vJ}$

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[DIFF] are calculated for each value of AJTT. This sum of differences expressed in the notation of the computer program is:

$$GVDIF = \sum_{v = MTRMIN(KI)}^{MTRIAL} DIFF \qquad (174)$$

The average difference is calculated in line (219) as the variable GVDA. The root mean square error, GVDF2, is calculated in lines 199 and 217 according to the formula:

$$GVDF2 = \left[\frac{\Sigma \; DIFF}{APLTST} \right]^{\frac{1}{2}} \qquad (175)$$

where APLTST is as defined in line 216.

The difference DIFB between B_v as calculated by Eq (172), and B_v as calculated by Eq (91) is obtained in line 202. This quantity is multiplied by 1000 and 1000*DIFB is the value printed in the output of the program.

The variable "NL" of lines 197 and 133 is a count of the total number of "v,J" combinations for which calculations are performed for one iteration of the FIPA. DO-loops 640 and 650 adjust the potential V(I) to reflect a new J(J+1) value for the next solution of the Schroedinger wave equation.

The average variance and the standard error of the fit used to obtain the "NPL" coefficients of the Legendre polynomials (Eqs (113) and (115)) for the "NL" combinations of "v,J" are calculated in lines 228 and 229.

On the first iteration, line 230 transfers the program to statement label 700 where the coefficients of the Legendre

polynomials of Eq (115) are calculated. The routine MATINV called by line 242 inverts the matrix AL(K,J) which then corresponds to the (X^TX) of Eq (13) and returns the inverted value in the same matrix. The MATINV routine, using the inverted AL(K,J) matrix and BL(K) calculates the coefficients of the Legendre polynomials of Eq (115), and returns the coefficients in the BL(K) array. DO-loop 720 then assigns the BL(K) coefficients to the array COEFF(K). DO-loops 740 and 760, then use the coefficients c_i [BL(k)] and the expectation value FX(K,I) to calculate the correction potential $\Delta V(r)$ of Eq (113). Then in the same line, a new corrected potential is obtained (Eq (110)).

The minimum of the potential curve is found (VMIN) and a new Y_{00} [YDH(1,1)] Dunham coefficient is calculated (line 253).

At this point, program control returns to statement label 253 for the "NREP"th iteration of the inverse perturbation routine.

On the second and following iterations, the program continues on from line 230. The standard error of E_{vJ} for all combinations of "v,J" is assigned to GVT. Using the coefficients COEFF(K) and the "error" ERROR(K) of the previous cycle (see DO-loop 720, DO-loop 680 prints the constants [DBAA] of the Legendre polynomials used to calculate ΔV , the standard error of that constant [T½ (line 236), and the ratio of the error to the constant, i.e., T/DBAA.

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After the last iteration, iteration number "NRPTT", line 241 transfers the program out of the loop which performs the IPA calculations. DO-loops 820 and 840 calculate the correlation coefficients for the Legendre polynomials (Eq (16)).

The routine POTTAB (called from line 264 of FIPA) then takes the potential energy curve generated by the IPA routine and produces the final set of turning points for the eigenvalues E_{vJ} of the routine and a second potential arranged in order of increasing "r" from P(I) minimum to P(I) maximum.

POTTAB starts by finding the minimum potential V(I) and assigns that value of "I" to IMIN. Next, starting with the inner portion of the adjusted IPA potential, from V(1) to V(IMIN), CALL PLLYNN finds the inner turning radii (AINN(I) for each of the eigenvalues E_{vJ} [EEE(I)] which were defined in line 203 of FIPA. PLLYNN obtains the turning points by doing a Lagrangian interpolation to the IPA potential. The process is repeated from V(IMIN) to V(M) for each EEE(I) to obtain the turning points on the outer portion of the IPA potential. The vibrational quantum numbers, v[IA], the energy eigenvalues [EEE(I)], the inner and outer turning points [AINN(I) and AOUT(I)], and the corresponding B_v [BBB(I)] values are printed.

POTTAB then using the new IPA potential, P(I) and V(I), where I=I,M, and the original RKR curve XI(I) and Yi(I) where I-1,N, determines an "IPA" potential energy for

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each RKR turning point, XI(I), by interpolation of the IPA curve. The difference in RKR and IPA energies for that radius is calculated.

Next POTTAB estimates the standard error of the potential for each value of "r" [XI(I)]. This standard error is based upon Eq (110):

$$V(r) = V(r) + \Delta V_0 (r) \tag{110}$$

The validity of the calculation used, is based upon the assumption that the routine has converged within some acceptable error limits to some $V(r)$. Any error in $V(r)$ is then associated with calculation of $\Delta V(r)$. The correction ΔV to the energy potential has been obtained using the Legendre polynomials of Eq (154). From the errors of the coefficients "c_i" used to calculate the correction potential, the error of the correction can be estimated. DO-loop 99 calculates the estimated standard error of the potential and prints it, the potential, the turning point, the difference between the RKR and IPA potential and the standard error of the potential.

Control of the program is returned from POTTAB to FIPA. FIPA prints out a summary of the sum of the differences for each value of J(J+1) calculated on each IPA iteration. It also prints out the average errors for all values of J(J+1) for each iteration. The program last of all prints

out the original Dunham coefficients with the new Y_{00} which has been calculated to set the minimum of the potential energy curve to zero.

This completes the description of the RKR-IPA program for one of set data. Control is then passed back to MAIN. If new data is provided, the RKR-IPA calculations are repeated for the new data.

To avoid any loss of information, Vida's original comments on input and output are included in this appendix with the revised program.

```
    1        1.          PROGRAM MAIN
    2              C AMUS:  GCR.JLININD
    3              C       MAIN PROGRAM: RIPA SYSTEM
    4              C
    5              C       THIS PROGRAM IS A UNIFICATION OF THE RKR AND IPA PROGRAMS WHERE
    6              C       THE RKR POTENTIAL IS USED AS AN INITIAL POTENTIAL IN THE IPA
    7              C       PROCEDURE.
    8              C
    9              C       RIPA CONSTRUCTS A POTENTIAL CURVE FOR AN ELECTRONIC STATE OF A
   10              C       ROTATIONLESS DIATOMIC MOLECULE -- I.E., PAIRS OF INNER AND OUTER
   11              C       CLASSICAL TURNING POINTS AND ASSOCIATED ENERGY LEVELS -- FROM
   12              C       DUNHAM EXPANSION COEFFICIENTS BY USING THE RYDBERG-KLEIN-REES
   13              C       METHOD. IT THEN PERFORMS AN EXTRAPOLATION OF THE INNER AND OUTER
   14              C       TURNING POINTS. FINALLY, RIPA PERFORMS AN INVERTED PERTURBATION
   15              C       APPROACH WHERE THE MEASURED TERM VALUES ARE FITTED TO THE QUANTUM
   16              C       MECHANICAL ENERGY EIGENVALUES OF A ROTATING VIBRATOR BY MEANS OF
   17              C       A LEAST SQUARES FIT USING A VARIATIONAL METHOD.
   18              C
   19              C       THE INPUT CARD DECK OF THE PROGRAM RIPA MUST BE AS FOLLOWS.
   20              C
   21              C       THE FIRST CARD HAS ITEST IN COLUMN 1.  IF ITEST = 0, THE
   22              C       PROGRAM WILL STOP.  IF ITEST = 1, THE PROGRAM WILL START A
   23              C       COMPLETE CALCULATION SEQUENCE, AND THE DATA DECK MUST BE AS
   24              C       FOLLOWS.
   25              C
   26              C       THE NEXT TWO CARDS HAVE THE OUTPUT PAGE TITLE IN COLUMNS 1
   27              C       THROUGH 72.
   28              C
   29              C       THE NEXT CARD HAS IIMS,THE VALUES OF THE MASSES OF THE TWO ATOMS
   30              C       AND THE IDENTIFICATION CODE OF THE ELECTRONIC STATE UNDER STUDY
   31              C       IN FORMAT I4,2D16.9,32X,A4. THE VALUES OF THE MASSES SHOULD BE
   32              C       EXPRESSED IN ATOMIC UNITS.  IIMS MUST BE 1 IF THE CARBON SCALE
   33              C       IS USED AND MUST BE 2 IF THE OXYGEN SCALE IS USED.  THERE IS AN
   34              C       OPTIONAL WAY OF USING THIS MASS CARD.  INSTEAD OF LISTING THE
   35              C       MASSES OF THE TWO ATOMS SEPARATELY, THE REDUCED MASS OF THE
   36              C       MOLECULE (IN ATOMIC UNITS) MAY BE ENTERED IN THE FIRST MASS FIELD
   37              C       THE SECOND MASS FIELD MUST THEN BE LEFT BLANK. THE CHOICE OF
   38              C       CARBON OR OXYGEN SCALE MUST, OF COURSE, STILL BE ENTERED.
   39              C
   40              C       THE NEXT CARD READS NDUN,(JM(I),I=1,NDUN) IN FORMAT 11I5. THE
   41              C       NDUN VALUES OF JM: N1, N2, N3, .... SPECIFY THE NUMBER OF DUNHAM
   42              C       COEFFICIENTS Y(I,1), Y(I,2), Y(I,3), ....
   43              C       THE NEXT CARDS CONTAIN THE DUNHAM COEFFICIENTS Y(I,K) WHICH ARE
   44              C       READ IN GOING FROM I=1 TO NDUN: (Y(I,1),I=1,N1), (Y(I,2),I=1,N2),
   45              C       (Y(I,3),I=1,N3),...... IN FORMAT (4D18,9).
   46              C
   47              C       THE NEXT CARD CONTAINS THE DISSOCIATION ENERGY DE AND THE ELEC-
   48              C       TRONIC TERM TE IN FORMAT 2015.8 AND EXPRESSED IN RECIPROCAL
   49              C       CENTIMETERS.  DE IS THE ENERGY SEPARATION BETWEEN THE POTENTIAL
   50              C       MINIMUM OF THE ELECTRONIC STATE UNDER STUDY AND ITS DISSOCIATION
   51              C       LIMIT. TE IS THE ENERGY SEPARATION BETWEEN THE POTENTIAL MINIMA
   52              C       OF THE ELECTRONIC STATE UNDER STUDY AND OF THE GROUND ELECTRONIC
   53              C       STATE OF THE MOLECULE.IF THE ELECTRONIC STATE UNDER STUDY IS
   54              C       ITSELF THE GROUND STATE, THIS CARD MUST BE BLANK.
   55              C
   56              C       THE NEXT CARD CONTAINS VFIN, AND VINC IN FORMAT 2F5.2. RIPA CAL-
   57              C       CULATES INNER AND OUTER TURNING POINTS FOR V = -0.25 AND FOR
   58              C       EACH VALUE OF V FROM ZERO TO VFIN IN STEPS OF VINC. IT IS NOT
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59    C    NECESSARY THAT VFIN, AND/OR VINC BE INTEGRAL. THE QUANTITY
60    C    VFIN/VINC MUST NOT EXCEED 399.
61    C
62    C    THE NEXT CARD IS THE KLEIN ACTION INTEGRAL PRINT SWITCH AND
63    C    CONTAINS IOPFG IN FORMAT I1. IT IS USED IN GENERATING THE
64    C    INITIAL RKR POTENTIAL. IF IOPFG=1, THE VALUES OF THE KLEIN ACTION
65    C    INTEGRALS ARE PRINTED FOR ALL OF THE ITERATIONS ASSOCIATED WITH
66    C    EACH OF THE VALUES OF V FOR WHICH PAIRS OF TURNING POINTS ARE
67    C    CALCULATED.  IF IOPFG=0, THESE VALUES ARE NOT PRINTED.
68    C
69    C    THE NEXT CARD CONTAINS RLIM1, RLIM2, AND NEXT IN FORMAT 2F6.2,I2.
70    C    RLIM1 AND RLIM2 ARE THE INNER AND OUTER LIMITS, RESPECTIVELY,
71    C    TO WHICH EXTENSIONS OF THE RYDBERG-KLEIN-REES TURNING POINTS
72    C    WILL BE ESTIMATED, IN A FASHION TO BE DESCRIBED BELOW. THE
73    C    INPUT QUANTITY NEXT IS THE NUMBER OF EXTRA EXTENSION DATA
74    C    POINTS TO FOLLOW. NEXT MAY NOT EXCEED 25 AND MAY BE ZERO, IF
75    C    NO EXTRA DATA POINTS ARE TO BE ADDED.
76    C
77    C    THE NEXT NEXT CARDS EACH CONTAIN R1(I) AND PE1(I) IN FORMAT
78    C    2D15.9. THE R1(I) AND PE1(I) ARE R AND POTENTIAL ENERGY PAIRS
79    C    WHICH MAY BE USED TO GUIDE THE EXTENSION TO THE RYDBERG-
80    C    KLEIN-REES TURNING POINTS, AS DESCRIBED BELOW. THE UNITS OF
81    C    THE R1(I) AND PE1(I) SHOULD BE ANGSTROMS AND RECIPROCAL
82    C    CENTIMETERS, RESPECTIVELY. NOTE....IF NEXT IS ZERO, THESE
83    C    CARDS MUST BE OMITTED FROM THE INPUT DECK.
84    C
85    C    THE NEXT CARD CONTAINS THE FITING PARAMETERS KFIT(I),I=1,2 AND
86    C    KOUT(I),I=1,4 IN FORMAT 6I5. IF THE CARD IS BLANK THE PROGRAM
87    C    TAKES THE DEFAULT VALUES 2, 4, 0, 6, 5,10. FOR EXTRAPOLATING THE
88    C    INNER TURNING POINTS KFIT(1) CONSTANTS INSIDE AN EXP-FUNCTION
89    C    OF THE FORM EXP(A(1)+A(2)*X+...) ARE USED WHICH ARE DETERMINED
90    C    BY A LEAST SQUARES FIT OF THE KFIT(1)+2 INNERMOST RKR TURNING
91    C    POINTS. FOR EXTRAPOLATING THE OUTER TURNING POINTS KFIT(2) CON-
92    C    STANTS ARE USED IN A FUNCTION OF THE FORM SUM(A(K)*R**(-KOUT(K)))
93    C    WHERE KOUT SPECIFIES THE INVERSE POWERS OF THE INTERNUCLEAR DIS-
94    C    TANCE R IN THE LONG RANGE INTERACTION FUNCTION. THE CONSTANTS ARE
95    C    DETERMINED BY A LEAST SQUARES FIT OF THE KFIT(2)+4 OUTERMOST RKR
96    C    TURNING POINTS.
97    C
98    C    THE NEXT DATA CARD IS THE PUNCH CONTROL CARD AND CONTAINS IPNRKR
99    C    AND IPNIPA IN FORMAT 2I2. IF IPNRKR=1, AN OUTPUT DATA DECK (RKR)
100   C    IS PUNCHED. IF IPNIPA=1, AN OUTPUT DATA DECK (IPA) IS PUNCHED.
101   C
102   C    THE NEXT CARD HAS LTEST IN COLUMN 1. IF LTEST=0, THE VARIATIONAL
103   C    PROCEDURE IS SKIPPED AND THE PROGRAM RETURNS TO THE BEGINNING TO
104   C    RESUME THE NEXT PROBLEM BY READING ITEST (SEE ABOVE).
105   C
106   C    IF LTEST=1, THE FOLLOWING ADDITIONAL CONTROL CARDS ARE NEEDED TO
107   C    RUN THE INVERTED PERTURBATION APPROACH.
108   C
109   C    THE NEXT CARD CONTAINS CONTROL VARIABLES FOR SCHR AS FOLLOWS--
110   C    NI,NS,IPSIQ,MAXIT, AND EPS IN FORMAT 4I4,D10.3.
111   C    IF NI = 1 DATA FROM EACH ITERATION IS PRINTED.
112   C    IF NI = 0 THE ITERATIONS ARE NOT PRINTED.
113   C    IF NS = 1 THE WAVE FUNCTIONS ARE PRINTED AT EVERY IPSIQ POINTS.
114   C    IF NS = 0 THE WAVE FUNCTIONS ARE NOT PRINTED.
115   C    EPS IS THE CONVERGENCE CRITERION.  0.001 WAVENUMBERS IS A GOOD
116   C    STARTING VALUE.
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117     C     MAXIT IS THE MAXIMUM NUMBER OF TIMES SCHR WILL ATTEMPT TO SATISFY
118     C     THE CONVERGENCE CRITERION.  TEN IS A GOOD STARTING VALUE.
119     C
120     C     THE NEXT CARDS CONTAIN RMIN,RMAX,M,NRPTT,NPL,MCH,LSW
121     C     AND (MTRMIN(I),MTRIAL(I),BJTT(I),I=1,11)
122     C     IN FORMAT 2F10.5,5I5/5(I2,I5,F5.3)/3(I2,I5,F5.0).
123     C     RMIN AND RMAX ARE THE LOWER AND UPPER LIMITS OVER WHICH THE
124     C     POTENTIAL CURVE IS TO BE CONSIDERED IN THE IPA PROCEDURE.
125     C     M IS THE NUMBER OF POINTS TO BE USED IN THE INTERPOLATED WELL
126     C     MAXIMUM M IS 2401
127     C     NRPTT DEFINES THE NUMBER OF ITERATIONS FOR THE INVERTED PERTURBA-
128     C     TION APPROACH, WHERE THE LAST ITERATION CALCULATES THE ROTATION-
129     C     LESS POTENTIAL FOR THE DEFINITION OF THE GV AND BV.
130     C     NPL IS THE ORDER OF THE CORRECTION FUNCTION OF THE POTENTIAL
131     C     WHICH IS DESCRIBED BY A SUM OF LEGENDRE POLYNOMIALS.
132     C     MTRMIN AND MTRIAL ARE THE MINIMUM AND MAXIMUM VALUE OF V+1 FOR
133     C     WHICH TRIAL VALUES ARE GENERATED (USING THE DUNHAM COEFFICIENTS)
134     C     FOR CALCULATING THE SCHROEDINGER EQUATION. THE PROGRAM STOPS
135     C     AUTOMATICALLY AT THE LAST BOUND STATE.
136     C     BJTT ARE THE VALUES OF J(J+1) FOR WHICH THE POTENTIAL  IS CALCU-
137     C     LATED.
138     C     FOR MCH=1 THE PROGRAM PUNCHES A DECK OF ALL THE GV AND BV VALUES
139     C     CALCULATED IN THE LAST ITERATION.
140     C     FOR LSW=2 THE PROGRAM PRINTS THE FIRST AND LAST ITERATION OF THE
141     C     INVERTED PERTURBATION APPROACH. FOR LSW=1 ALL ITERATIONS ARE
142     C     PRINTED.
143     C
144     C     THIS COMPLETES THE INPUT DATA DECK FOR ONE ELECTRONIC STATE.
145     C     THERE ARE NOW TWO OPTIONS.  IF NO OTHER POTENTIAL CURVES ARE TO
146     C     BE CALCULATED, A BLANK CARD MUST BE AT THE END OF THE DATA DECK,
147     C     I.E., ITEST=0.  IF A SECOND INPUT DATA DECK IS TO FOLLOW FOR
148     C     ANOTHER ELECTRONIC STATE, THE ABOVE INSTRUCTIONS SHOULD BE
149     C     REPEATED, I.E., ITEST=1.
150     C
151     C     THE FOLLOWING COMMENTS APPLY TO THE PRINTED OUTPUT OF RIPA.
152     C
153     C     THE FIRST LISTING STARTS WITH THE TITLE AND THE IDENTIFICATION
154     C     NUMBER OF THE ELECTRONIC STATE. THE VALUES OF THE ATOMIC MASSES
155     C     (OR THE VALUE OF THE REDUCED MASS OF THE MOLECULE) ARE ALSO
156     C     PRINTED AND THE CHOICE OF CARBON OR OXYGEN SCALE IS NOTED.  THE
157     C     LISTING ALSO CONTAINS THE RESULTS OF THE RKR CALCULATIONS. FOR
158     C     EACH VALUE OF V IN STEPS OF VINC UP TO VFIN, THE POTENTIAL AND
159     C     INERTIAL ENERGIES, THE INNER AND OUTER TURNING POINTS, AND THE
160     C     FINAL VALUES OF THE KLEIN ACTION INTEGRALS ARE LISTED.  THE
161     C     POTENTIAL ENERGY IS THE EXPANSION FOR GV + Y(J,3) EVALUATED AT
162     C     V. THE INERTIAL ENERGY IS THE EXPANSION FOR BV EVALUATED AT V.
163     C     BOTH ARE EXPRESSED IN RECIPROCAL CENTIMETERS.  THE TWO TURNING
164     C     POINTS ARE EXPRESSED IN ANGSTROMS.  THIS LISTING WILL ALSO
165     C     INCLUDE THE INTERMEDIATE VALUES OF THE KLEIN INTEGRALS IF
166     C     IJPFG=1.
167     C
168     C     THE SECOND LISTING CONTAINS THE PARAMETERS THAT PERTAIN TO THE
169     C     FIT OF THE INNER AND OUTER EXTENSIONS OF THE RKR POTENTIAL.
170     C     FOR THE FUNCTIONS INDICATED ABOVE THE LISTING GIVES THE CONSTANTS
171     C     AND THEIR STANDARD ERRORS AND THE TOTAL STANDARD ERROR. IT SHOWS
172     C     THE FIT FOR THE EXTENSION OF THE INNER AND OUTER TURNING POINTS.
173     C     FINALLY, IF EXTRA EXTENSION DATA POINTS ARE USED, THE DIFFERENCES
174     C     BETWEEN THESE AND THE FIT FUNCTION ARE GIVEN FOR EACH OF THE
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175        C    INPUT R1(1).
176        C    FURTHERMORE, THE DUNHAM COEFFICIENTS ARE LISTED WITH THE CALCU-
177        C    LATED VALUE Y(0,0).
178        C
179        C    THE FOLLOWING PRINTOUT EXCEPT FOR THE DUNHAM COEFFICIENTS DOES
180        C    NOT APPEAR IF LTEST=0.
181        C
182        C    THE FOLLOWING LIST PRESENTS THE PARAMETERS OF THE INVERTED PER-
183        C    TURBATION APPROACH.
184        C
185        C    THE PROGRAM THEN GENERATES A PRINTOUT OF THE FIRST AND LAST ITE-
186        C    RATION OF THE INVERTED PERTURBATION APPROACH AND A PRINTOUT OF
187        C    THE INTERMEDIATE ITERATIONS IF LSW = 1. FOR EVERY VALUE OF BJIT
188        C    IT GENERATES A TABLE WHICH CONTAINS FOR ALL VALUES OF V SPE-
189        C    CIFIED BY MTRMIN AND MTRIAL, THE QUANTUM MECHANICAL ENERGY EIGEN-
190        C    VALUE, THE MEASURED TERM VALUE, THE DIFFERENCE, THE CALCULATED
191        C    BV VALUE, THE DIFFERENCE TO THE MEASURED VALUE AND THE VALUES
192        C    OF THE WAVE FUNCTIONS FOR THE INNERMOST AND OUTERMOST MEMBERS
193        C    OF THE ARRAY S. MA AND MB ARE DETERMINED BY THE SCHROEDINGER
194        C    ROUTINE SUCH THAT S(MA) AND S(MB) ARE TYPICALLY 1.D-10 IF THE
195        C    LIMITS RMIN AND RMAX ARE MADE WIDE ENOUGH.
196        C    FOR THE LAST ITERATION THE TABLE CONTAINS VIBRATIONAL LEVELS
197        C    ABOVE THE UPPER DASHED LINE AND BELOW THE LOWER DASHED LINE WHICH
198        C    WERE NOT SPECIFIED BY THE DATA FIELD ABOVE, BUT WHICH ARE UNIQUE-
199        C    LY SPECIFIED BY THE RANGE OF INTERNUCLEAR DISTANCES WHICH HAD TO
200        C    BE ADJUSTED IN THE INVERTED PERTURBATION APPROACH.
201        C    THE MEASURED VALUES ARE THOSE DEFINED BY THE DUNHAM COEFFICIENTS.
202        C    EVERY TABLE IS CLOSED WITH THE AVERAGE DEVIATION AND THE STANDARD
203        C    ERROR IN CM**(-1).
204        C
205        C    AFTER EVERY ITERATION THE PROGRAM PRINTS THE COEFFICIENTS OF THE
206        C    LINEAR COMBINATION OF LEGENDRE POLYNOMIALS OBTAINED IN THE IN-
207        C    VERTED PERTURBATION APPROACH. IT ALSO LISTS THE STANDARD ERROR
208        C    AND THE RELATIVE STANDARD ERROR. IF THE LATTER QUANTITY IS LARGER
209        C    OR COMPARABLE TO 1 AFTER THE FIRST ITERATION, NPL CAN BE LOWERED
210        C    IN THE NEXT RUN OF THE PROGRAM. THE LAST SET OF COEFFICIENTS IS
211        C    FOLLOWED BY THE CORRESPONDING CORRELATION MATRIX.
212        C
213        C    THE NEXT LISTING GIVES THE INTERPOLATED INNER AND OUTER TURNING
214        C    POINTS AND THE BV VALUES FOR THE CALCULATED QUANTUM MECHANICAL
215        C    ENERGY EIGENVALUES OF THE ROTATIONLESS MOLECULE AS OBTAINED AFTER
216        C    THE LAST ITERATION.
217        C
218        C    THE FINAL LISTING CONTAINS A TABULATION OF THE ENTIRE POTENTIAL
219        C    WELL. THESE DATA ARE (1) THE TURNING POINTS AND ENERGIES FORM THE
220        C    LAST IPA ITERATION, (2) THE DIFFERENCE TO THE INITIAL RKR POTEN-
221        C    TIAL AND (3) THE CORRESPONDING STANDARD ERROR OF THE POTENTIAL.
222        C    IN ADDITION, IT CONTAINS THE 20 INNER AND 99 OUTER EXTENSION
223        C    POINTS FROM THE EXTRAPOLATION METHOD DESCRIBED ABOVE. THE 20
224        C    INNER EXTENSION POINTS ARE EQUALLY SPACED IN R BETWEEN RLIM1 AND
225        C    THE INNERMOST RKR TURNING POINT, AND THE 99 OUTER EXTENSION
226        C    POINTS ARE EQUALLY SPACED IN R BETWEEN THE OUTERMOST RKR TURNING
227        C    POINT AND RLIM2. ALL UNITS ARE ANGSTROMS AND RECIPROCAL CENTI-
228        C    METERS.
229        C
230        C    THE PRINT OUT CLOSES WITH A RECOMMENDED SET OF INTEGRATION LIMITS
231        C    RMIN AND RMAX AS OBTAINED IN THE IPA PROCEDURE. THEY SHOULD BE
232        C    USED IN THE FOLLOWING RUNS. IT IS FOLLOWED BY A SUMMARY OF THE
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233      C       STANDARD ERRORS OF ALL ITERATIONS AND A TABLE OF THE DUNHAM COEF-
234      C       FICIENTS WITH A CORRECTED VALUE OF Y(0,0) SUCH THAT THE POTENTIAL
235      C       MINIMUM DEFINES ZERO ENERGY.
236      C
237      C       THIS COMPLETES THE PRINTED OUTPUT FOR ONE ELECTRONIC STATE.  IF
238      C       DATA FOR MORE THAN ONE STATE ARE INCLUDED IN THE INPUT DECK, THE
239      C       ABOVE OUTPUT IS REPEATED.
240      C
241      C       THE FOLLOWING COMMENTS APPLY TO THE PUNCHED OUTPUT OF RKR.
242      C
243      C       IF IPHRKR=1 AND/OR IPNIPA=1, A DECK IS PUNCHED WHICH IS TAILORED
244      C       TO SERVE AS INPUT TO OTHER PROGRAMS. ALL UNITS ARE ATOMIC MASS
245      C       UNITS (CARBON SCALE), ANGSTROMS, OR RECIPROCAL CENTIMETERS.
246      C       FOR IPHRKR=1 ONE OBTAINS THE RKR-POTENTIAL.
247      C       FOR IPNIPA=1 ONE OBTAINS THE IPA-POTENTIAL.
248      C
249      C       THE FIRST CARD CONTAINS THE REDUCED MASS OF THE MOLECULE
250      C       (AND EXPRESSED IN ATOMIC MASS UNITS, CARBON SCALE) AND ICODE IN
251      C       FORMAT 36X,D16.9,16X,A4.
252      C       THE NEXT CARD READS NDUN,(JN(I),I=1,10) IN FORMAT 1115. THE NDUN
253      C       VALUES OF JN: N1, N2, N3, .... SPECIFY THE NUMBER OF DUNHAM
254      C       COEFFICIENTS Y(1,1), Y(1,2), Y(1,3), ....(AS EXPLAINED ABOVE)
255      C
256      C       THE NEXT CARD CONTAINS DE AND TOE IN FORMAT 2D15.8.  DE IS THE
257      C       ENERGY SEPARATION BETWEEN THE BOTTOM OF THE ROTATIONLESS
258      C       POTENTIAL WELL OF THE ELECTRONIC STATE UNDER STUDY AND ITS
259      C       DISSOCIATION LIMIT.  TOE IS THE ENERGY SEPARATION BETWEEN THE
260      C       BOTTOM OF THE ROTATIONLESS POTENTIAL WELL OF THE NEUTRAL OR IONIC
261      C       ELECTRONIC STATE UNDER STUDY AND THE V=0, J=0 LEVEL OF THE
262      C       GROUND ELECTRONIC STATE OF THE NEUTRAL MOLECULE.  NOTE.... IF
263      C       ELECTRONIC STATE UNDER STUDY IS ITSELF THE GROUND STATE OF THE
264      C       NEUTRAL MOLECULE, THEN TOE=-T(0,0).
265      C
266      C       THE NEXT CARD CONTAINS N IN FORMAT I3, WHICH IS THE NUMBER OF R
267      C       AND POTENTIAL ENERGY PAIRS TO FOLLOW.
268      C
269      C       THE NEXT N CARDS CONTAIN THE R AND POTENTIAL ENERGY PAIRS WITH
270      C       TWO PAIRS PER CARD IN FORMAT 2D16.9,4X,2D16.9. THE DATA ON THESE
271      C       CARDS IS THAT TABULATED IN THE FIRST TWO COLUMNS OF THE THIRD
272      C       OUTPUT LISTING.
273      C
274      C       THIS COMPLETES THE PUNCHED OUTPUT FOR ONE ELECTRONIC STATE.  IF
275      C       DATA FOR MORE THAN ONE STATE ARE INCLUDED IN THE INPUT DECK, THE
276      C       ABOVE OUTPUT IS REPEATED.
277   2.         DIMENSION KIMS(2),ZIMS(2),NFI(2),LOUT(4),IHEAD(36)
278   3.         COMMON/RPO/R1(25),PE1(25),NEXT
279   4.         COMMON/YD/YDH(20,10),JN(10)
280   5.         COMMON/FC/F(11),G(11),RE,RAA,RUB,KFIT(2),KOUT(4)
281   6.         COMMON/EX/EV(921),UV(921),M
282   7.         DATA KIMS/4HC=12,4HO=16/
283   8.         DATA NFI/ 2, 4/
284   9.         DATA LOUT/ 4, 6, 8, 10/
285   10.        DATA ZIMS/ 1.0, 3.9976221165/
286      C       RKR USES THE FOLLOWING FACTORS FOR CONVERTING BETWEEN MASS SCALES
287      C       AND DIFFERENT PHYSICAL UNITS.
288      C       ZIMS(2) IS 15.99491464/16, WHICH IS THE MASS OF OXYGEN ON THE
289      C       CARBON SCALE DIVIDED BY THE MASS OF OXYGEN ON THE OXYGEN SCALE.
290      C       FACNU =SQRT(H-BAR*AVOGADROS NUMBER/(4*PI*C))*10**8
```

```
    1            PROGRAM MAI
    2       C       RKR1H1.1  C, 1C D'C .5-2
    3            DIMENSION ZIMS(2),NFT(2),LCUT(4),IHEAD(36)
    4            COMMON/RPW/R1(25),PE1(25),NEXT
    5            COMMON/YD/YDH(20,10),IV(10)
    6            COMMON/FC/F(11),H(11),RF,RAA,RHH,KFIT(2),KCUT(4)
    7            COMMON/EX/EV(521),LV(521),M
    8            CHARACTER KIMS(2)*4
    9            DATA (KIMS(I),I=1,2)/'C=12','C=16'/
   10            DATA NFT/ 2, 4/
   11            DATA LCUT/ C, 6, 8,10/
   12            DATA ZIMS/ 1.0, 0.99946+2165/
   13       C       RKR USES THE FOLLOWING FACTORS FOR CONVERTING BETWEEN
   14       C       MASS SCALES AND DIFFERENT PHYSICAL UNITS.  ZIMS(2) TO
   15       C       15.99451464/16, WHICH IS THE MASS OF OXYGEN ON THE CARBON SCALE
   16       C       DIVIDED BY THE MASS OF OXYGEN ON THE OXYGEN SCALE.
   17       C       FACNUM=SQRT(H-BAR*AVOGADROES NUMBER/(4*PI*C))*10**8
   18            FACNUM=4.105404548
   19       C      ........READ IN INPUT DATA
   20      10    READ 109,ITEST
   21            IF(ITEST.EQ.C) STOP
   22            READ 110,IHEAD
   23            READ 111,IIMS,ZMAS1,ZMAS2,ICODE
   24            IF((IIMS.NE.1).AND.(IIMS.NE.2)) IIMS=1
   25       C      ........PUT REDUCED MASS INTO ZMU
   26            ZMU=ZMAS1
   27            IF(ZMAS2.GT...) ZMU=ZMAS1*ZMAS2/(ZMAS1+ZMAS2)
   28            ZMU=ZMU*ZIMS(IIMS)
   29            FAC=FACNUM/SQRT(ZMU)
   30            CALL YDHF11(3)
   31            HE = YDH(1,2)
   32            RE=FAC/SQRT(HE)
   33            READ 112,DE, E
   34       C      .........CALCULATE YDD
   35            A2=-YDH(2,2)*YDH(2,1)/(12.CD+D+H)
   36            YDH(1,1)=(BE+YDH(3,1))/4.0D+0+A2+A2*A2/BF
   37            READ 113,VFIN,VINC
   38            READ 109,ICFFG
   39            READ 113,RLM1,RLM2,NEXT
   40       C      .........READ EXTRA EXTENSION DATA IF NECESSARY
   41            IF (NEXT.LE.25) GO TO 20
   42            PRINT 103
   43            STOP
   44      20    IF (NEXT.LT.1) GO TO 40
   45            DO 30 I=1,NEXT
   46      30    READ 104,R1(I),PE1(I)
   47      40    READ 118,(KFIT(I),I=1,2),(KCUT(I),I=1,4)
   48            DO 50 I=1,2
   49            IF(KFIT(I).EQ.0) KFIT(I) =NFT(I)
   50            IF(KFIT(I).GT.11) KFIT(I)=11
   51      50    CONTINUE
   52            DO 60 I=1,4
   53            IF(KOUT(I).EQ.C) KCUT(I) = LCUT(I)
   54      60    CONTINUE
   55            READ 109,IFNFKR,IFNIFA
```

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```
56        C         ..........F-INT CUT THE INPUT DATA
57                  FRINT 114,IHEAD
58                  PRINT 115,ICODE
59        C         ..........FRINT THE PASSES AND THEIR UNITS
60                  IF (ZMAS2.LE.0.0) GO TC 70
61                  PRINT 116,KIMS(IIMS),ZMAS1,ZMAS2
62                  GO TO 80
63        70        PRINT 117,KIMS(IIMS),ZMAS1
64        80        PRINT 105,DE,TE
65                  FRINT 106,RLM1,RLMC,VFIN,VINC,ICPFG,IPARKP,IPAIPA
66        C         ..........FRINT EXTRA EXTENSION DATA IF NECESSARY
67                  IF(NEXT.LT.1) GO TC 90
68                  FRIN  107
69                  FPINT 108,(P1(I),FE1(I),I=1,NEXT)
70        90        CALL RKP(VFIN,VINC,ICPFG,FAC)
71                  CALL YDHP11(0)
72                  FRIN  114,IHEAD
73        C         ......EXTRAPOLATE FOR END POINTS OF POTENTIAL FUNCTION
74                  CALL EXTEND(FLM1,FLM2)
75                  M=2**+120
76                  IF(IPARKP.NE.1) GO TC 95
77        C         PUNCH 102,IIMS,ZMAS1,ZMAS2,ZMU,ICODE
78        C         CALL YDHP11(IFARKP)
79        C         FUNCH,112,CE,TE
80        C         FUNCH 119,M
81        C         PUNCH 120,(EV(I),UV(I),I=1,M)
82        95        FRIN: 121
83                  CALL FIPA(ZMU,CE)
84                  CALL YDHP11(0)
85                  IF (IPNIPA.NE.1) GO TC 10
86        C         PUNCH 102,IIMS,ZMAS1,ZMAS2,ZMU,ICODE
87                  CALL YDHP11(IPNIPA)
88        C         FUNCH 112,CE,TE
89        C         PUNCH 119,M
90        C         PUNCH 120,(EV(I),UV(I),I=1,M)
91                  GO TC 10
92        102       FORMAT (I4,3D16.5,16X,A4)
93        103       FORMAT(37HOTOO MANY EXTRA EXTENSION DATA POINTS)
94        104       FORMAT (2D16.5)
95        105       FORMAT(//6H CE = ,D15.7,10X,6H TE = ,D15.7/)
96        106       FORMAT(2X,*LIM1 = *,F5.4,* LIM2 = *,F5.4,* VFIN = *,F7.2,
97                 +* VINC = *,F7.2//*  ICPFG = *,I1,* IPARKP = *,I1,
98                 +* IPNIPA = *,I1/)
99        107       FORMAT(*  THE FOLLOWING DATA WE'E INCLUDED IN THE LEAST-SQUARED
100                +FIT THAT DETERMINED THE COEFFICIENTS OF THE XIEN-*/*
101                + SICN FUNCTION  TO THE PK' TURNING POINTS..*//
102                +10X,*R*,15X,*FOTENTIAL ENERGY */)
103       108       FORMAT(4X,1FD16.9,7X,D16.9/)
104       109       FORMAT(2I2)
105       110       FORMAT(1H,A4)
106       111       FORMAT(I4,2D16.9,32X,A4)
107       112       FORMAT(2D15.9)
108       113       FORMAT(2F6.2,I2)
109       114       FORMAT(2X,1HA4/2X,18A4)
110       115       FORMAT(//*  THE CODE NUMBER FCF THIS STATE IS *,A4)
111       116       FORMAT(//*THE MASSES OF THE TWO ATOMS,*/* MASED ON *,A4,* AF *,
112                +1PD16.9,*  AND *,D16.9/)


113       117       FORMAT(//*  THE REDUCED MASS OF THE TWO ATOMS,BA ED ON  *,A4,*
114                + IS *,1FD16.9)
115       118       FORMAT(1C15)
116       119       FORMAT(I3)
117       120       FORMAT(2D16.9,4X,2D16.9,4F)
118       121       FORMAT(*  BEGINNING OF INVERTED PERTUBATION AFPROACH *//)
119                 END
```

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```
    1              SUBROUTINE RKR(VFIN,VINC,ICPFG,FAC)
    2        C        RKR PROCEDURE
    3              DIMENSION BI(101),TEMP(400),DPTQ(M),MZ(3),IZ(3),XG(4),YG(4)
    4              DOUBLE PRECISION AGAUS(3,4),XGAUS(3,4)
    5              COMMON/YD/YDM(20,10),IM(10)
    6              COMMON/EX/EV(921),UV(921),M
    7              COMMON/RX/RMIN(400),RMAX(400),U(400)
    8        C      ........INTEGRATION CONSTANTS(ABROMOWITZ,P.921)
    9        C        THE XGAUS ARE THE ABSICCISAS AND AGAUS ARE THE WEIGHTING FACTOR
   10        C        FOR A GAUSSIAN INTEGRATION OF MOMENTS WHERE N=? ARE THE
   11        C        4,6, OR 8 DEPENDING ON THE DEGREE OF SUCCES OF THE
   12        C        ITERATION.
   13              DATA XGAUS/0.0194557717512320D0,0.0337652428962424D0,1. 93451-44?
   14             +0297400,
   15             +0.1016667612931860D0,0.1693953067666D D0,0.23 00547852275710,
   16             +0.2372337950411360D0,0.3165850406195412D0,0.6699950521732423D0,
   17             +0.4068282676752175D0,0.6193050593041557D0,0.9335E6F15777 2.20?,
   18             +0.5917173212477525D0,0.7306046932331320D0,0.601,0.76276620495P1640?,
   19             +0.9662347571015760D0,0.0D0,0.8953332327069140?,0.00,0.00,0.933144?
   20             +928287670D0,
   21             +0.0D0,0.0D0/
   22              DATA AGAUS/0.0506142681451680D0,0.0356622461659500,0.173 374.256-7
   23             +27D0,
   24             +0.1111905172266870D0,0.1003807865240730,0.3280705774312770,
   25             +0.1568533229384440D0,0.2339569672463450,0.3240727744312770,
   26             +0.1813418916951410C0,0.2339569672463450,0.1735274225667270C,
   27             +0.1913418916951810D0,0.1603078652407000,0.00,0.1566F332 2?5 44? ,
   28             +0.0356622461659500,0.0D0,0.1111905172266670,0.00,0.00,0.55614
   29             +266145188D0,
   30             +0.0D0,0.0D0/
   31              DATA MZ/101,61,61/
   32              DATA IZ/8,6,4/
   33        C      ..CALCULATE TEMP(THE V) AND U(THE GV) FOR EACH TURNING POINT
   34              M=VFIN/VINC+0.5D0
   35              M=M+2
   36              IF(M.LE.400) GO TO 100
   37              IVINC=100./(VFIN/3.5+1.)
   38              VINC=1./FLOAT(IVINC)
   39              M=VFIN/VINC + 2.5
   40              PRINT 291,VINC
   41        100   TEMP(1)=0.25D+0
   42              U(1)=POLYN(TEMP(1),1)
   43              DO 110 I=2,M
   44              TMP=FLOAT(I-2)*VINC+0.5D0
   45              TEMP(I)=TMP
   46        110   U(I)=POLYN(TMP,1)
   47              STEP=.9D0
   48              PRINT 294
   49        C        COMMENCE FINDING TURNING POINTS BY INTEGRATION AND
   50        C      ITERATE TO A BUILT IN LIMIT OF PRECISION
   51              SVTR=0.0
   52              VTR=0.0D0
   53              SETR=POLYN(VTR,1)
   54              IF (ABS(SETR).LT.1.D-8) GO TO 130
   55              VTR=-YDM(1,1)/YDM(2,1)
```

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56                ETR=POLYN(VTR,1)
57       120      IF (ABS(ETR).LT.1.0C-4) GO TO 130
58                XTR=SVTR-(SETR*(SVTR-VTP))/(SETR-ETR)
59                SVTR=VTR
60                VTR=XTR
61                SETR=ETR
62                ETR=POLYN(XTR,1)
63                GO TO 120
64       130      VMINS=VTR-0.5
65                DO 240 I=1,N
66                VMIN=VMINS+0.5
67                FEG=0.0C
68                GEG=0.0D0
69                LT=1
70                IGD=0
71                IFD=0
72       140      HS=VMIN+(TEMP(I)-VMIN)*STEP
73                IF(LT.GT.3) GO TO 180
74                MQ=NZ(LT)
75                KM=MQ-2
76                A=(HS-VMIN)/FLOAT(MQ-1)
77                DO 160 J=1,MQ
7                 UV(J)=VMIN+FLOAT(J-1)*A
78                EV(J)=POLYN(UV(J),1)
80                IF (IGD.EQ.0) BI(J)=POLYN(UV(J),2)
81                DENG(I)=U(I)-EV(J)
82                UV(J)=1.0C/SQRT(ABS(DENG(I)))
83       160      EV(J)=BI(J)*UV(J)
84                FSUM=UV(1)+4.D0*UV(MQ-1)+UV(MQ)
85                GSUM = EV(1) + 4D0*EV(MQ-1) + EV(MQ)
86                DO 170 J=2,KM,2
87                FSUM=FSUM + 4.D0*UV(J) + 2.D0*UV(J+1)
88       170      GSUM = GSUM + 4.D0*EV(J) + 2.D0*EV(J+1)
89                FEG2=A*FSUM/3.D0
90                GEG2=A*GSUM/3.D0
91                IF (LT.GT.1) GO TO 250
92                GO TO 260
93       180      IZDO=(LT-1)/3
94                IF(IZDO.GT.3) IZDO=3
95                NGAS=IZ(IZDO)
96                DO 190 J=1,NGAS
97                XG(J)=(HS-VMIN)*XGALS(IZDO,J) +VMIN
98       190      UV(J)=XG(J)
99                EPSH = TEMP(I) -XG(NGAS)
100               IF(EPSH.LE.0.) GO TO 270
101               DO 200 K=1,NGAS
102      200      DENQ(K)=POLYN(TEMP(I),1)-POLYN(XG(K),1)
103               IF (IGD.NE.0) GO TO 220
104               DO 210 J=1,NGAS
105      210      BI(J)=POLYN(UV(J),2)
106      220      FSUM=0.0D0
107               GSUM=0.0D0
108               DO 240 J=1,NGAS
109               IF (DENQ(J).LE.0.) GO TO 270
110               XG(J)=AGALS(IZDO,J)/SQRT(DENG(J))
111               YG(J)=BI(J)*XG(J)
112               FSUM=FSUM+XG(J)
```

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113        240  GSUM=GSUM+YG(J)
114             HS1=HS-VFIN
115             FEG2=PSV-FSUM
116             GEG2=BSV+GSUM
117        C          CHECK IF ITERATION CRITERION IS MET
118        C          IT MAY HAVE TO BE ADJUSTED IN STATEMENTS 250
119        C       FOR PROPER CONVERGENCE WHEN RUN ON OTHER MACHINES
120        250  IF ((FEG2/FEG).LE.5.0-7) IFD=1
121             IF ((GEG2/GEG).LE.5.0-7) IGD=1
122             IF (ABS(FEG2/FEG1).GT.0.9) IFD =1
123             IF (ABS(GEG2/GEG1).GT.0.9) IGD=1
124        260  LT=LT+1
125             FEG1=FEG2
126             GEG1=GEG2
127             IF (IFD.EQ.0) FEG = FEG + FEG2
128             IF (IGD.EQ.0) GEG = GEG + GEG2
129             IF ((IFD.NE.0).AND.(IGD.NE.0)) GO TO 270
130             VFIN=HS
131        C          IF INTERMEDIATE EVALUATIONS OF KLEIN ACTION INTEGRALS
132        C          ARE TO BE OUTPUT THEN WRITE OUT THE FEG AND GEG
133             IF (IOPFG.NE.0) PRINT 295,FEG,GEG
134             IF (LT.LE.20) GO TO 140
135             PRINT 297
136             RETURN
137        270  F=FEG+FAC
138             EF=GEG/FAC
139             RMAX(I)=SQRT(F+F+F/GF)+F
140             RMIN(I)=RMAX(I)-2.00+F
141        C          WRITE OUT THE TURNING POINTS AND THE
142        C          CORRESPONDING KLEIN ACTION INTEGRALS
143             TEMP(I)=TEMP(I)-0.5
144             PRINT 296,TEMP(I),U(I),BI(NGAS),RMIN(I),RMAX(I),F,EF
145        280  CONTINUE
146        C       .........END OF INTEGRATION AND ITERATION LOOP
147             RETURN
148        291  FORMAT(1X,*VFIN, AND VINC GIVE MORE THAN ONE TURNING POINT PAIR
149            +--INCREMENT HAS BEEN ADJUSTED TO VINC= *,F5.2)
150        294  FORMAT( / * POTENTIAL GENERATED BY PKP IS AS FOLLOWS*//12X,
151            +*POTENTIAL*,10X,*INERTIAL*,5X,*KLEIN ACTION INTEGRALS*//*    V*,*
152            +,*ENERGY*,13X,*ENERGY*,15X,*RMIN*,1-X,*RMAX*,16X,*F*,1-X,*EF*/)
153        295  FORMAT(6X,*FEG = *,D16.6,*, GEG = *,D16.6)
154        296  FORMAT(1X,F5.2,F15.4,D22.9,F16.9,F20.9,3X,2D20.9)
155        297  FORMAT(* LT REACH MAXIMUM VALUE OF 20--RK9 INTEGRATION ITER-A
156            +TION NOT LIKELY TO SUCCEED. *)
157             END




                     FUNCTION POLYN(X,A)
1
2          C          SUBROUTINE FOR PKP SYSTEM
3          C          SOLVES FOR ROOTS OF POLYNOMIAL FUNCTIONS OF TYPE
4          C       POLYN=SUM FOR I=1 TO IM(N) OF Y(I,N)+X++(I+1)
5                COMMON/YD/Y(20,10),IM(10)
6                POLYN=0.
7                J=IM(N)
8                IF (J.EQ.0) RETURN
9                S=1.
10         10   DO 10 I=1,J
11              POLYN= POLYN +Y(I,N)+S
12         10   S=S+X
13              RETURN
14              END
```

COMPARABLE MAP--(C-A)

```
1              SUBROUTINE EXTEND(PLM1,PLM2)
2        C        SUBROUTIN FOR RKR SYSTEM
3        C        RCUTINE FOR FINDING INNERMOST 20 POINTS AND CUTERMCST 33 POINTS
4        C        OF POTENTIAL FUNCTION BY EXTRAPOLATION.  THIS RCUTINE ALSO
5        C        REORDEPS THE POINTS DEFINING THE POTENTIAL FUNCTICN IN ASCENDING
6        C        MAGNITIUDE OF R (THE INTERNUCLEAR DISTANCE).
7              COMMON/GL/X(928),Z(828),L
8              COMMON/RPW/R1(25),PE1(25),NEXT
9              COMMON/FC/F(11),B(11),PE,RAA,RBB,NIN,NCUT,LCUT(4)
10             COMMON/EX/XO(921),YC(921),N
11             COMMON/RX/RMIN(400),RMAX(400),U(400)
12             DO 10 I=1,11
13       10    B(I) =0.
14       C     .........SPECIFIY LIMITS OF FIT FUNCTION
15             RAA=RMIN(N) - 1.0-8
16             RBB=RMAX(N) +1.0-8
17       C     .........FIR OF THE INNER TURNING POINTS
18             L=NIN + 2
19             DC 2C I = 1,L
20             X(I) = RMIN(N-I+1)
21       20    Z(I)= ALOG10(U(N-I+1))
22             IF (NEXT.EG.3) GO TC 30
23             CO 25 I= 1,NEXT
24             IF (R1(I).EE.RAA) GC TO 25
25             L=L+1
26             X(L)=R1(I)
27             Z(L)= ALOG10(PE1(I))
28       25    CONTINUE
29       30    PRINT 92,RAA,NIN
30             PRINT 93
31             CALL GLSQ(1)
32       C     .........FIT CF THE OUTER TURNING POINTS
33             L=NCUT +4
34             DO 40 I= 1,L
35             X(I) = RMAX(N-I+1)
36       40    Z(I) = U(N-I+1)
37             IF (NEXT.EQ.C) GO TC 60
38             CO 50 I =1,NEXT
39             IF (R1(I).LE.RBB) GC TC 50
40             L=L+1
41             X(L)=R1(I)
42             Z(L) = PE1(I)
43       50    CONTINUE
44       60    PRINT 94,RBB,NCUT
45             PRINT 95
46             CALL GLSQ(2)
47       C     .........FINAL FIT CF THE POTENTIAL
48             F6 = (RMIN(N) - PLM1)/20.
49             DO 70 I=1,20
50             XMO=PLM1+FLOAT(I-1) +F6
51             XO(I) =XMO
52       70    YO(I) = FUNC(0,XMO)
53             DO 80 I=1,N
54             J=N-I+1
55             K = 20+I
```

```
56            XO(K) = RMIN(J)
57    PC      YO(K) = U(J)
58            DO 85 I=1,N
59            K= N+I+21
60            XO(K)= RMAX(I)
61    65      YO(K)= U(I)
62            K=N +21
63            XO(K)=RE
64            YO(K)= 0.000
65            F6 = (RLM2 -RMAX(N))/99.
66            DO 90 I=1,99
67            K=2*I +1+21
68            XMO = RMAX(N) +FLOAT(I)+F6
69            XO(K) =XMO
70    90      YO(K)=FUNC(O,XMO)
71            RETURN
72    92      FORMAT(*  FIT OF INNERMOST TURNING POINTS FOR EXTRAPOLATING U(R)
73           +WITH R LESS THAN *,1PD15.7,* USING *///*A FUNCTION OF THE FORM
74           +EXP(B(1)+B(2)+X+B(3)+X+X....+B(K)+X++(K-1)) WITH K=NTM= *,I2/)
75    93      FORMAT(12X,*R*,15X,*LOG(U(R))*,13X,*FCALC*,15X,*DIFF*/)
76    94      FORMAT(*  FIT OF OUTERMOST TURNING POINTS FOR EXTRAPOLATING U(R)
77           +WITH R GREATER THAN *,1PD15.7,* USING *///*A FUNCTION OF THE FORM
78           +B(1)+B(2)+R++(-6)+B(3)+R++(-3)+....+B(K)+...WITH K=KNOTS *,I2/)
79    95      FORMAT(12X,*R*,15X,*U(R)*,15X,*FCALC*,15X,*DIFF*/)
80            END
```

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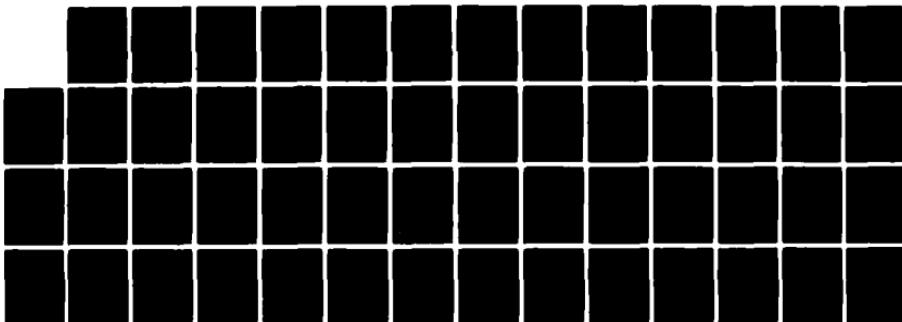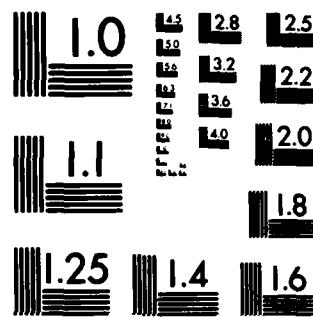
MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

```
1         SUBROUTINE GLSQ(KK)
2      C      GENERAL LEAST SQUARES ROUTINE TO FIT A SET OF N DATA POINTS
3      C      KK=1: FIT RKR TURNING POINTS BY LEGENDRE POLYNOMIALS
4      C      KK=2: FIT INNER TURNING POINTS BY EXPONENTIAL FUNCTIONS
5      C      KK=3: FIT OF OUTER TURNING POINTS BY SUM OF C(N)*EXP(-N)
6             DIMENSION T(11)
7             COMMON/GL/X(828),Z(828),N
8             COMMON/FC/F(11),B(11),RE,RAA,RBB,NFIT(2),LCUT(4)
9             COMMON/TM1/A(64,64),BB(64)
10            M=NFIT(KK)
11     C      .............INITIALIZATION
12     10     DO 20  J=1,M
13            BB(J)=0.0D0
14            DO 20 K=1,M
15     20     A(J,K)=0.0D0
16     C      .............CALCULATION OF THE MATRIX
17            DO 30 I=1,N
18            DUMMY=FUNC(KK,X(I))
19            DO 30 J=1,M
20            BB(J)= BB(J)+Z(I)*F(J)
21            DO 30 K=1,M
22     30     A(J,K)=A(J,K)+F(J)*F(K)
23            CALL MATINV(DETERM,M,1,0)
24            DO 40 I=1,M
25            NC=I
26            IF (KK.GT.1) NC=NFIT(1) + I
27     40     B(NC) = BB(I)
28     C      .........CALCULTION OF FIT AND STANDARD ERROR
29            SIG =0.0
30            DO 50 I=1,N
31            XCRY =X(I)
32            DUMMY=FUNC(KK,XCRY)
33            DEL=Z(I) - DUMMY
34            PRINT 104,XCRY,Z(I),DUMMY,DEL
35     50     SIG=SIG+DEL*DEL
36            SIGMA=SQRT(SIG/FLOAT(N-M))
37     C      .............ITERATION TEST
38            IF (M.LE.2) GO TO 60
39            DRDH =ABS(SQRT(ABS(A(M,M)))/BB(M))*SIGMA
40            IF ((SIGMA.GT.1D-3).AND.(DRDH.LT.0.7)) GO TO 60
41            M=M-1
42            NFIT(KK) = M
43            GO TO 10
44     C      ...........PRINT OUT OF CONSTANTS AND ERRORS
45     60     PRINT 101
46            DO 70 I=1,M
47            T(I)=SQRT(ABS(A(I,I)))*SIGMA
48            DRDB= ABS(T(I)/BB(I))
49     70     PRINT 102, I,BB(I),T(I),DRDB
50            PRINT 103, N, SIGMA
51     101    FORMAT(*  CONSTANTS OF FIT*/)
52     102    FORMAT(*  B(*,I2,* ) =*,D15.7,5X,*RMS ERROR = *,D15.7,5X,*RELATIVE
53            +RMS ERROR =*,D15.7)
54     103    FORMAT(//*NUMBER OF ENTRIES : *,I3,* STANDARD ERROR = *,1PD14.5/)
55     104    FORMAT (1F22.9,3D20.9)
```

```
56            RETURN
57            END
```

```
     1          SUBROUTINE MATINV(DETERM,N,M,IPV)
     2    C        MATRIX INVERSION WITH ACCOMPANYING SOLUTICN CF LINEAR EQUATIONS
     3    C        IPV.EQ.1: NO SEARCH FOR PIVOT,IPV.NE.1: SEARCH FOR PIVOT
     4    C        IMPLICIT DOUBLE PRECISION (A-H,C-Z)
     5          DIMENSION IPIVOT(64),INDEXR(64),INDEXC(64)
     6          COMMON/TM1/A(64,64),B(64,1)
     7    C        ...............INITIALIZATION
     8          DETERM=1.0
     9          DO 20 J=1,N
    10    20    IPIVOT(J) =0
    11          DO 550 I=1,N
    12          IF (IPV.NE.1) GO TO 40
    13          ICLM = I
    14          GO TO 260
    15    C        ...................SEARCH FOR PIVOT ELEMENT
    16    40    AMAX = 0.0
    17          DO 105 J = 1,N
    18          IF (IPIVOT(J).EQ.1) GO TO 105
    19    C        FOR UNSYMMETRIC MATRIX: A(I,J).NE.A(J,I)
    20    C          DO 100 K=1,N
    21    C        FOR SYMMETRIC MATRIX:  A(I,J).EQ.A(J,I)
    22          DO 100 K=J,N
    23          IF (IPIVOT(K).EQ.1) GO TO 100
    24          IF (ABS(AMAX).GE.ABS(A(J,K))) GO TO 100
    25          IROW =J
    26          ICLM=K
    27          AMAX=A(J,K)
    28    100   CONTINUE
    29    105   CONTINUE
    30          IPIVOT(ICLM) = IPIVOT(ICLM) + 1
    31          INDEXR(I) = IROW
    32          INDEXC(I) = ICLM
    33    C        ......INTERCHANGE ROWS TO PUT PIVOT ELEMENT ON DIAGONAL
    34          IF (IROW.EQ.ICLM) GO TO 260
    35          DETERM = -DETERM
    36          DO 200 L = 1,N
    37          SWAP = A(IROW,L)
    38          A(IROW,L) = A(ICLM,L)
    39    200   A(ICLM,L) = SWAP
    40          IF (M.LE.0) GO TO 260
    41          DO 250 L=1,M
    42          SWAP = B(IROW,L)
    43          B(IROW,L)=B(ICLM,L)
    44    250   B(ICLM,L) = SWAP
    45    260   PIVOT = A(ICLM,ICLM)
    46          IF (N.GT.10) GO TO 330
    47          DETERM = DETERM*PIVOT
    48    C        .........DIVIDE PIVOT ROW BY PIVOT ELEMENT
    49    330   A(ICLM,ICLM) = 1.0
    50          DO 350 L=1,N
    51    350   A(ICLM,L) =A(ICLM,L)/PIVOT
    52          IF (M.LE.0) GO TO 380
    53          DO 370 L =1,M
    54    370   B(ICLM,L)=B(ICLM,L)/PIVOT
    55    C        .........REDUCE NON-PIVOT ROWS
```

```
56        3-0   DO 550 L1=1,N
57              IF (L1.EQ.ICLM) GO TO 550
58              =A(L1,ICLM)
59              A(L1,ICLM) =0.0
60              DO 450 L= 1,
61        450   A(L1,L) = A(L1,L)-A(ICLM,L)*
62              IF (M.LE.0) GO TO 550
63              DO 500 L=1,M
64        500   B(L1,L) = B(L1,L) - A(ICLM,L)*
65        550   CONTINUE
66              IF (IPV.EQ.1) RETURN
67    C         ...........INTERCHANGE COLUMNS
68              DO 710 I = 1,N
69              L= N+1-I
70              IROW = INDEXR(L)
71              ICLM = INDEXC(L)
72              IF (IROW.EQ.ICLM) GO TO 710
73              DO 705 K =1,N
74              SWAP=  A(K,IROW)
75              A(K,IROW) = A(K,ICLM)
76        705   A(K,ICLM) =SWAP
77        710   CONTINUE
78              RETURN
79              END
```

B-66

```
1          FUNCTION FUNC(KK,XX)
2      C      ROUTINE DEFINES THE LEGENDR POLYNOMIALS FOR FITTING THE RK
3      C      POTENTIAL AND CONTAINS THE TWO EXTRAPOLATION FUNCTION  BEYON
4      C      THE INNERMOST AND OUTERMOST TURNING POINTS, RESPECTIVELY.
5          COMMON/FC/F(11),B(11),RE,RAA,RBB,NIN,NOUT,LCUT(4)
6          COMMON/EX/XI(921),YI(921),N
7          IF((XX.LT.RAA).OR.(KK.EQ.1)) GO TO 60
8          IF ((XX.GT.RHB).OR.(KK.EQ.2)) GO TO 80
9      C      ..........FUNCTION FOR RKR TURNING POINTS
10         NPOLY = 8
11         FUNC= 0.0
12         NM = (NPOLY +1)/2
13         NM1 = NM +1
14         NUP = N + NM1 -NPOLY
15         DO 20 J = NM1,NUP
16         IF (XX.LE.XI(J)) GO TO 30
17   20    CONTINUE
18         J=NUP
19   30    L=J-NM
20         LLL= L+ NPOLY -1
21         DO 50 K = L,LLL
22         TERM = 1.0
23         DO 40 M = L,LLL
24         IF (K.EQ.M) GO TO 40
25         TERM = TERM* (XX-XI(M))/(XI(K)-XI(M))
26   40    CONTINUE
27         TERM = YI(K)*TERM
28   50    FUNC= FUNC + TERM
29         RETURN
30   C      ..........FUNCTION FOR INNER TURNING POINTS
31   60    X = (RE-XX)/RE
32         F(1) = 1.0
33         FUNC = F(1) *B(1)
34         DO 70 I = 2,NIN
35         F(I) = F(I-1)*X
36   70    FUNC = FUNC + F(I)*B(I)
37         IF (KK.EQ.1) RETURN
38         FUNC = 10.**FUNC
39         RETURN
40   C      ..........FUNCTION FOR OUTER TURNING POINTS
41   80    X =1./XX
42         FUNC = 0.0
43         DO 90 I = 1,NOUT
44         F(I) = X**LCUT(I)
45   90    FUNC =   FUNC + F(I)*B(NIN+I)
46         RETURN
47         END
```

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```
1          SUBROUTINE YDHFIL(NSW)
2     C        PRINT,PUNC AND READ SUBROUTINE OF DUNHAM COEFFICIENTS
3     C        (NSW.LE.0) PRINT, NSW=1:PRINT AND PUNCH, NSW=2; READ AND
4     C        PRINT, (NSW.GE.3):READ
5          COMMON/YD/YDH(20,10),JM(10)
6          IF (NSW.LT.2) GO TO 40
7     C        ................INITIALIZATION
8          DO 10 IDH = 1,10
9          JM(IDB) = 0
10         DO 10 IDA = 1,20
11    10   YDH(IDA,IDH)= 0.
12    C        ..................READ INSTRUCTIONS
13         READ 101,NDUM,(JM(I),I=1,NDUM)
14         DO 20 IDN=1,NDUM
15         NGBD = JM(IDN)
16         IF (NGBD.EQ.0) GO TO 30
17    20   READ 102,(YDH(I,IDN),I=1,NGBD)
18    30   CONTINUE
19         IF (NSW.GT.2) RETURN
20    C        .........PRINT INSTRUCTIONS
21    40   PRINT 103
22         DO 60 IDN = 1,20
23         NMX =0
24         DO 50 IY = 1,10
25         IF (JM(IY).GE.IDN) NMX = IY
26    50   CONTINUE
27         IF (NMX.EQ.0) GO TO 70
28    60   PRINT 104,(YDH(IDN,I),I=1,NMX)
29    70   IF (NSW.NE.1) GO TO 90
30    C        .........PUNCH INSTRUCTIONS
31    C        PUNCH 101,NDUN,(JM(I),I=1,NDUN)
32    C        DO 80 IDN =1,NDUN
33    C        NGBD = JM(IDN)
34    C 80  PUNCH 102,(YDH(I,IDN),I= 1,NGBD)
35    90   CONTINUE
36         RETURN
37    101  FORMAT (14I5)
38    102  FORMAT (4D18.9)
39    103  FORMAT (*   THE DUNHAM COEFFICIENTS */)
40    104  FORMAT (1X,1P8D16.8)
41         END
```

```fortran
        SUBROUTINE F?PA(?MU,DE)
C          ROUTINE RUNNING INVERTED PERTUBATION APF CACH
        DIMENSION GVSUM(10),FFL(64),MTEMIN(11),PCUT(11),YMAX(11),HJT (11),
     +   MTRIAL(11),GVST(11,10),LTPIAL(11),ER(11),COFFF(64),FRROR(64),
     +   FX(11,2403),KA(11,98),KH(11,98)
        COMMON /EX/XI(921),YI(921),N
        COMMON /A2/V(2403)
        COMMON/A3/F(2403)
        COMMON /A4/ (2403)
        COMMON/AN2/MA,MB
        COMMON/AN4/ETRIAL(100),RTRIAL(100),AJTT, TRIAL,KV(100)
        COMMON/YD/YOM(20,10),JM(10)
        COMMON/TM1/AL(64,64),BL(64)
        COMMON/PL/YPL(64),AA1,AA2,AA3, PL
        COMMON/PO/AINN(100),AOUT(100),EEE(100),BNH(100)
        INTEGER SCHP
C          THE ATOMIC UNITS USED INTERNALLY IN THIS PROGRAM ARE DEFINED
C          BY THE FOLLOWING CONSTANTS.
C          FACMN = RYDBERG CONSTANT*MASS OF THE ELECTRON IN AMU.
C          AZERO = BOHR RADIUS
C          FACRT= SQRT(H-EAR*AVOGADRO-NUMBER/(4*P I*C)*10**5
        AZERO= 0.52917706
        ZIRA = 1.0/AZERO
        FACMN=60.19972628
        FACM=FACMN/ZMU
        ZIEN = 1.0/FACM
        FACRT=4.105804549
        READ 3003, LTEST
        IF (LTEST .EQ. 0) RETURN
C          ......READ CONTROL VARIABLES FOR SCHROEDINGER ROUTINE
        READ 3005, NI,NS,IPSIQ,MAXIT,EPSC
        EPS = EPSC*ZIEN
        READ 3004,RMIN,RMAX,M,NRPTT,NPL,MCH,LSW
        READ 3021,(MTRMIN(I),MTPIAL(I),HJTT(I),I=1,11)
        IF ((M.EQ.0).OR.(M.GT.2403)) M=2403
        IF ((NPL.EQ.0).OR.(NPL.GT.31)) NPL=31
        IF ((NRPTT.EQ.0).OR.(NRPTT.GT.6)) NRPTT =6
        DO 80 J= 1,11
        DO 80 I=1,98
        KA(J,I) =0
80      KB(J,I)= 0
        NTT =0
        DO 100 IDA = 1,10
        IF (BJTT(IDA).LT.1.D-06) GO TO 120
100     NTT = NTT + 1
120     IF (NTT.EQ.0) NTT = 1
        ABE = YOM(1,2)
        CBE =ABE*ZIEN
        RRE = FACRT/SQRT(ZMU*ABE)
        CRE= RRE/AZERO
        IF (XI(1).GT.RMIN) RMIN = XI(1)
        IF ((XI(N).LT.RMAX).OR.(RMAX.LT.0.001)) RMAX =XI(N)
        RH = (RMAX-RMIN)/FLOAT(M-1)
        DO 140 J =1,M
        P(J) = FLOAT(J-1)*RH + RMIN
```

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```
56              140   V(J) = FUNC(C,P(J))
57                    NT1=NTT +1
58                    BJTT(NT1) =C.
59                    DO 180 KI = 1,NT1
60                    NTRIAL = 99
61                    AJTT = BJTT(KI)
62        C     .........SEARCH FOR CENTRIFUGAL BARTER
63                    TX = 0.
64                    ASX= 1.D+70
65                    DO 160 I=1,M
66                    SX = V(I) + ABE*(RRE/P(I))**2*AJTT
67                    IF (SX.LT.ASX) GO TO 160
68                    IF (SX.LE.TX) GO TO 160
69                    TX = SX
70                    ROUT(KI) = P(I)
71                    YMAX(KI)=SX
72              160   ASX=SX
73                    CALL BETRL(TX)
74                    LTRIAL(KI)=NTRIAL
75                    IF (MTRIAL(KI).GT.NTRIAL) MTRIAL(KI) = NTRIAL
76                    NTRIAL = MTRIAL(KI)
77              180   ER(KI) = ETRIAL(NTRIAL)
78        C     ......SEARCH FOR INNERMOST AND OUTERMOST TURNING POINTS
79                    N3A=M
80                    N3B=0
81                    DO 240 KI = 1,NTT
82                    N3AA = M
83                    N3BB = 0
84                    ASX = 1.D+70
85                    DO 200 I = 1,M
86                    SX = V(I) + ABE*(RRE/P(I))**2*BJTT(KI)
87                    IF ((SX.LE.ER(KI)).AND . (ASX.GE.ER(KI))) N3AA = I
88                    IF ((SX.GE.ER(KI)).AND.(ASX.LE.ER(KI))) N3BB = I
89                    IF (N3BB.GT.0)GO TO 220
90              200   ASX = SX
91              220   IF (N3AA.LE.N3A) N3A = N3AA
92                    IF (N3BB.GE.N3B) N3B = N3BB
93              240   CONTINUE
94                    RMII = P(N3A)
95                    RMAA= P(N3B)
96                    DO 260 KI = 1,NT1
97                    AJTT = BJTT(KI)
98                    NTRIAL = LTRIAL(KI)
99                    TX =V(N3B) + AHE*(RRE/RMAA)**2*AJTT
100                   IF(RMAA.GT.RCUT(KI)) TX = YMAX(KI)
101                   SX = V(N3A) + ABE * (RRE/RMII)**2*AJTT
102                   IF (SX.LT.TX) TX =SX
103                   CALL BETRL(TX)
104                   LTRIAL(KI) = NTRIAL
105                   IF (NTRIAL.LT.MTRIAL(KI)) LTRIAL(KI) = MTRIAL(KI)
106             260   CONTINUE
107                   NREP =1
108                   PRINT 3000,,RMII,RMAX,RH,EPSC,NRPTT,RMII,RMAA,PPE,NPL
109                   RMIN = RMIN +ZIRA
110                   PMAX = RMAX+ZIRA
111                   PM = RM+ZIRA
112                   AA1 = ZIRA*((RMAA+RMII)*PPE-2.*RMAA*RMII)/(RMAA-RMII)
```

```
113                  AA2= (RMAA+RMII-2.+KFE)/(RMAA-RMII)
114                  AA3 = ZIPA+K°E
115                  DO 270 I = 1.M
116                  P(I) = P(I)+ZIPA
117                  CALL PLEGEN(P(I))
118                  DO 270 J = 1.NFL
119          270     FX(J,I) = YPL(J)
120                  N3A = M
121                  N3B=0
122          260     ISW=LSW
123                  IF ((NREP.EQ.1).OR.(NREP.EQ.NRPTT)) ISW=1
124                  NT3 = NT1
125                  IF (NREP.EQ.NRPTT) GO TO 320
126          C       ..........INITIALIZATION
127                  DO 300 I = 1.NPL
128                  BL(I)= 0.0
129                  DO 300 J=1,NFL
130          300     AL(I,J)= 0.0
131                  NT3 = NTT
132          320     GVTT2 = 0.
133                  NL= 0
134                  DO 340 I = 1,M
135          340     V(I) =(V(I)-DE)+ZIEN + CRE+((CRE/P(I))++2+HJT°(1)
136                  DO 660 KI = 1,NT3
137                  NTRIAL = MTRIAL(KI)
138                  NTRMIN = MTRMIN(KI)
139                  IF (NREP.LT.NRPTT) GO TO 360
140                  NTRIAL = LTRIAL(KI)
141                  NTRMIN = 1
142          360     AJTT = BJTT(KI)
143                  TX = 1.CD+10
144                  CALL RETRL(TX)
145                  LJT = SQRT(AJTT)
146                  IF (ISW.EG.1) PRINT 3007,AJTT,LJT
147                  KLIM = 2
148                  LLK = 0
149                  KLK = 0
150                  GVDIF = 0.
151                  GVDF2=  0.
152          C       ...........DO SCHRJEDINGER LOOP
153                  DO 600 I = NTRMIN,NTRIAL
154                  ETRIAL(I) = (ETRIAL(I) - DE)+ZIEN
155                  ECALC = ETRIAL(I)
156                  MA = KA(KI,I)
157                  MB = KB(KI,I)
158                  IF (SCHR(NI,NS,MAXIT,EPS,IPSIQ,M,RMIN,RMAX,KV(I),ECALC,FACM)-1)420
159                 +,400,380
160          380     KLK =  KLK +1
161                  IF (KLK.LT.KLIM) GO TO 420
162                  PRINT 3010
163                  CALL EXIT
164          400     LLK =LLK +1
165          420     IF (MA.LT.N3A) N3A = MA
166                  IF (MB.GT.N3B) N3B = MB
167                  KA(KI,I) = MA
168                  KB(KI,I) = MB
169                  HCALC = (S(1)/P(1))++2 + 4.+(S(2)/P(2))++2 + (S(M)/P(M))++2
```

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```
170                      KSIPP = M-1
171               DO 440 J=3,KSIPP,2
172         440   BCALC=2.*(S(J)/P(J))**2 + 4.*(S(J+1)/P(J+1))**2 +BCALC
173               BCALC = FACM*BCALC*PH/3.
174               ECALC = DE + ECALC*FACM
175               ETRIAL(I)=ETRIAL(I)*FACM + DE
176               DIFF = ETRIAL(I) - ECALC
177               IF(NREP.EQ.NRPTT) GC TC 540
178               DO 460 K = 1,NPL
179         460   FPL(K) = 0.0
180               DO 490 J = MA,MB
181               AJ = 4 + (J/2)*4 -2*J
182               DO 490 K = 1,NPL
183         490    FPL(K) = FPL(K) + AJ*S(J)**2*FX(K,J)
184         490   CONTINUE
185               DO 500 K = 1,NPL
186         500    FPL(K) = FPL(K)*RH/3.
187   C     ....................................................................
188   C     STATISTICAL WEIGHT EWG
189         EWG = 1.0
190   C     ....................................................................
191               DO 520 K = 1,NPL
192               BL(K) = BL(K) + DIFF*FPL(K)*EWG
193               DO 520 J=1,NPL
194         520   AL(K,J) = AL(K,J) + FPL(J)*FPL(K)*EWG
195         540   IF ((I.LT.MTRMIN(KI)).OR.(I.GT.MTRIAL(KI)).OR.(KI.EQ.NT1))GO TO 56
196             +
197               NL= NL + 1
198               GVDIF = GVDIF + DIFF
199               GVDF2 = GVDF2 + DIFF*DIFF
200               GVTT2 = GVTT2 + DIFF*DIFF*EWG
201         560   IF (ISW.EQ.0) GO TO 600
202               DIFR = (BTRIAL(I) -BCALC) *1000.0
203               EEE(I) = ECALC
204               BBB(I)= BCALC
205               IF ((NREP.LT.NRPTT).OR.(KI.EQ.NT1)) GO TO 580
206               IF (I.EQ.MTRMIN(KI)) PRINT 3020
207   C     ...............PRINT SCHROEDINGER RESULTS
208         580   PRINT 3008,KV(I),ECALC,ETRIAL(I),DIFF,BCALC,DIFR,S(MA),S(MB),MA,MB
209               IF ((NREP.LT.NRPTT).OR.(KI.EQ.NT1)) GO TO 600
210               IF (I.EQ.MTRIAL(KI)) PRINT 3020
211         600   CONTINUE
212               IF ((NREP.LT.NRPTT).OR.(MCH.NE.1)) GO TO 620
213   C         PUNCH 3018,NTRMIN,NTRIAL
214   C         PUNCH 3019,(KV(I),EEE(I),BBB(I),AJTT,I=NTRMIN,NTRIAL)
215         620 IF(LLK.GE.1) PRINT 3009,LLK
216               APLTST = MTRIAL(KI) - MTRMIN(KI) + 1
217               GVDF2 = SQRT(GVDF2/APLTST)
218               GVST(KI,NREP) = GVDF2
219               GVDA = GVDIF/APLTST
220               IF (ISW.EQ.1) PRINT 3011,GVDIF,GVDA,GVDF2
221               DO 640 I = 1,M
222         640   V(I)= V(I) - CBE*(CRE/P(I))**2*AJTT
223               IF (KI.EQ.NT1) GO TO 660
224               AJTT= BJTT(KI+1)
225               DO 650 I = 1,M
226         650   V(I) = V(I) + CHE*(CRE/P(I))**2*AJTT
```

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```
227         660    CONTINUE
22P                GVTT2= GVTTO/FLCAT(NL-NPL)
229                GVSUM(NREP) = SQRT(GVTT2)
230                IF (NREP.EQ.1) GO TC 700
231                NRPI=NREP - 1
232                PRINT 3012,NRM1
233                GVT = GVSUM(NREP)
234                DO 680 K= 1,NPL
235                OBAA = COEFF(K)
236                T = SQRT(ERRCR(K))*GVT
237                TEPP = ABS(T/OHAA)
238         680    PRINT 3C13,K,OBAA,T,TEMP
239         700    DO 710 I = 1,M
240         710    V(I) = V(I)*FACM + DE
241                IF (NREP.EQ.NRPTT) GC TO P00
242                CALL MATINV(DETERM,NPL,1,0)
243                DO 720 K = 1,NPL
244                COEFF(K) = HL(K)
245         720    ERROR(K) = ABS(AL(K,K))
246         C      ...........CORRETCTION OF POTENTIAL AND YDH(1,1)
247                VMIN = 1.0D+10
24P                DO 760 I = 1,M
249                DO 740 K =1,NPL
250         740    V(I) = V(I) + HL(K)*FX(K,I)
251                IF (V(I).LT.VMIN) VMIN = V(I)
252         760    CONTINUE
253                YDH(1,1) = YDH(1,1) - VMIN
254                DO 780 I =1,M
255         780    V(I) = V(I) - VMIN
256                NREP = NREP + 1
257                GO TO 260
258         P00    PRINT 3001
259                DO 840 KE = 1,NPL
260                COEFF(KE) = SQPT(ABS(AL(KE,KE)))
261                DO 820 KEE = 1,KE
262         820    FPL(KEE)= (ABS(AL(KE,KEE))/COEFF(KE))/COEFF(KEE)
263         840    PRINT 3002,KE,(FPL(L),L=1,KE)
264                CALL POTTAB(GVT,AZERO,DE,M,NTRIAL)
265                PRINT 3014,N3A,P(N3A),N3B,P(N3B)
266                PRINT 3015
267                DO 860 I = 1,NTT
26·                PRINT 3016,BUTT(I),(GVST(I,L),L=1,NRPTT)
269         860    CONTINUE
270                PRINT 3020
271                PRINT 3017,(GVSUM(I),I=1,NPPTT)
272                RETURN
273         3001   FORMAT('1','   CORRELATION MATRIX OF THE COEFFICIENTS'//)
274         3002   FORMAT(/I5,10F10.6,4(/5X,10F10.6))
275         3C03   FORMAT(I1)
276         3004   FORMAT (2F10.0,6I5)
277         3C05   FORMAT (4I4,D10.0)
278         3006   FORMAT('  PMIN = ',F6.3,',  RAMAX = ',F6.3,'  SPACING = ',F10.7
279                +/' CONVERGENCE CRITERION IS ERROR LESS THEN ',C9.2/
2P0                +/' NUMBER OF ITERATICNS = ',I3//' PARAMETERS CF THE FITTING POLY''
2A1                +NIAL'//' RMIN = ',F7.3,'PMAX =',F7.3,' RE =',F7.3,'  NPL=',I3//)
282         3007   FORMAT (' RESULTS CF SCHROEDINGER EQUATION FCR J(J+1) =',F5.0
283                +,' AND J=',I3,//4X,'V     GV CAL     GV MEAS     GV M-C     JV CAL
```

```
284              *    HV  H-C    S(MA)     S(MH)    MA     MH */)
285       3008 FORMAT (1X,I4,2F12.5,F11.5,F13.3,F10.5,2(1PD10.1),2I6)
286       3009 FORMAT ('0  PROGRAM SUCCESSFUL. (MAXIT REACHED ',I2,' TIMES)')
287       3010 FORMAT ('   SCHR NOT SUCCESSFUL')
288       3011 FORMAT(//'  SUM OF DIFF.=',1PD12.4,'   AVERAGE DIFF. =',D12.4,'
289            *  RMS OF GV =',D12.4/)
290       3012 FORMAT ('0 COEFFICIENTS OF THE LEGENDRE POLYNOMIALS AFTER ITERATION
291            *N NO. ',I2/)
292       3013 FORMAT(' H(',I2,') =',1PD15.9,4X,'RMS ERROR =',D16.6,4X,'RELATIVE
293            *  RMS ERROR = ',D14.4)
294       3014 FORMAT(/ 'RECOMMENDED INTEGRATION LIMITS RMIN = R(',I4,') =', F6.'
295            *,'RMAX =R(',I4,')=',F7.3/)
296       3015 FORMAT (1H1,' SUMMARY OF ERRORS OF THE INVERTED PERTURBATION APP
297            *ACH '//3X,'J(J+1)',4X,'1.',9X,'2.',9X,'3.',8X,'4.',9X,'5.',8X,
298            *'6.',8X,'7.',8X,'8.',8X,'9.',7X,'10.ITERATION'/)
299       3016 FORMAT (1X,F8.1,10F10.5)
300       3017 FORMAT (/'  AVERAGE',10F10.5)
301       3018 FORMAT(2I10)
302       3019 FORMAT (I2,3D16.9)
303       3020 FORMAT (1X,57(2H--))
304       3021 FORMAT (6(I2,I3,F7.0)/5(I2,I3,F7.0))
305            END
```

```
    1              INTEGER FUNCTION SCH (NI,NS,MX,EPS,IPSIO,NN,RMIN,RMAX,KV,E ,FACM)
    2        C        SCHROEDINGER EQUATION SOLVING ROUTINE FOR PSI**2+(E-V)*P**=3
    3        C        NI=1  PRINT ITERATIONS, OTHERWISE NO PRINTOUT
    4        C        NS=1: PRINT SOLUTIONS WITH EACH ENERGY LEVEL, OTHE WISE NO PR.
    5              COMMON/A2/V(2403)
    6              COMMON/A4/S(2403)
    7              COMMON/AN2/MA,MB
    8              EPRIN = EC*FACM
    9              IF (NI.EQ.1) PRINT 201,KV,EPRIN
   10              H = (RMAX -RMIN)/FLOAT(NN-1)
   11              H2= H*H
   12              HV= H2/12.00
   13              E=EC
   14              TEST = -1.00
   15              DE = 0.00
   16        C     ...........DETERMINATION OF INNER INTEGRATION LIMIT
   17              DO 10 IPP = 1,NN
   18              LCRIT = IPP -1
   19              IF (V(IPP).LE.E) GO TO 13
   20        1C    CONTINUE
   21        13    KERR =1
   22              IF (LCRIT.LT.1) GO TO 83
   23              NL1 = LCRIT + 2
   24              WCRIT = 0.
   25              DO 16 IPP = 1,LCRIT
   26              LCT =LCRIT + 1 - IPP
   27              WCRIT = WCRIT + SQRT(V(LCT) - E)*H
   28              F (WCRIT.GE.20.0) GO TO 2C
   29        16    CONTINUE
   30        2C    MA = LCT
   31        C     ............DETERMINATION OF OUTER INTEGRATION LIMIT
   32              DO 23 IPP= 1,NN
   33              LCT = NN + 1 - IPP
   34              IF (V(LCT).LE.E) GO TO 26
   35        23    CONTINUE
   36        26    LCRIT = LCT +1
   37              KERR = 2
   38              IF (LCRIT.GT.NN) GO TO 83
   39              WCRIT = 0.
   40              DO 30 IPP = LCRIT,NN
   41              LCT = IPP
   42              WCRIT=WCRIT +SQRT(V(IPP) - E)*H
   43              IF (WCRIT.GE.20.0) GO TO 33
   44        3C    CONTINUE
   45        33    MB=LCT
   46              DO 35 IPP = NL1,NN
   47              IF (V(IPP).GT.E) GO TO 130
   48        35    CONTINUE
   49        130   NL2 = IPP
   50              DO 140 I = 1,MA
   51        140   S(I)=0.0
   52              DO 150 I = MB,NN
   53        150   S(I) = 0.0
   54              MAP1 = MA + 1
   55        C     ...........START ITERATION LOOP
```

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```
56            DO 60 IT = 1,MX
57        C   ...........START INWARD INTEGRATION
58            S(PB) = 1.D-10
59            GN = V(MB) - E
60            GI = V(MB-1) - E
61            RMOX = RMIN + H*FLOAT(MB-1)
62            S(MB-1) = S(MB)*EXP(RMOX*SQRT(GN)-(RMOX-H)*SQRT(GI))
63            YA = (1.D0 - HV*GN)*S(MB)
64            YB= (1.D0 - HV*GI)* S(MB-1)
65            M =MB-2
66        36  YC = YB + ((YB-YA) + H2*GI*S(M+1))
67            GI = V(M) -E
68            S(M) = YC/(1.D0-HV*GI)
69            KER  =3
70            IF (S(M).LT.0.0D0) GO TO 83
71            IF (S(M).LE.S(M+1))GO TO 40
72            YA = YB
73            YB = YC
74            M = M-1
75            GO TO 36
76        40  MSAVE = M
77            PM = S(M)
78            YIN = YB/PM
79            DO 43 J = M,MB
80        43  S(J)=S(J)/PM
81        C   ...........START OUTWARD INTEGRATION
82            S(MA) = 1.0D-10
83            YA=0.0D0
84            GI=V(MA) - E
85            YB = (1.D0-HV*GI)*S(MA)
86            DO 46 I = MA+1,M
87            YC = YB + ((YB -YA) + H2*GI*S(I-1))
88            GI = V(I) -E
89            S(I) = YC/(1.D0-HV*GI)
90            YA=YB
91        46  YB=YC
92            PM=S(M)
93            YOUT= YA/PM
94            YM=YC/PM
95            DO 50 J=MA,M
96        50  S(J)=S(J)/PM
97        C   ...........CORRECTION
98            DF = 0.0D0
99            DO 53 J=MA,MB
100       53  DF= DF - S(J)*S(J)
101           F = (-YOUT -YIN + 2.0D0*YM)/H2* (V(M) - E)
102           DOLD = DE
103           DE = -F/DF
104           IF (NI.NE.1) GO TO 56
105           EPRIN =E*FACM
106           DEPRIN = DE*FACM
107           PRINT 203,IT,EPRIN,F,DF,DEPRIN,MSAVE
108       56  EOLD =E
109           E=E +DE
110           TEMP = ABS(DOLD) -ABS(DE)
111           IF (TEMP.GT.TEST) TEST =TEMP
112           IF (TEST.LT.0.0D+0) GO TO 60
```

```
113             IF (AHS(E-EULD).LE.AHS(EPS)) GO TO 63
114      6(     CONTINUE
115             SCHR = 1
116             GO TO 66
117      C..............COUNT NODE'
118      63     SCHR = 0
119      66     KV = 0
120             DO 70 J = NL1,NL2
121             IF((S(J-1).LT.0.0).AND.(S(J).GE.0.0).AND.(S(J+1).GT.0.0)) KV=KV+1
122             IF((S(J-1).GT.0.0).AND.(S(J).LE.0.0).AND.(S(J+1).LT.0.0)) KV=KV+1
123      70     CONTINUE
124      C      ............NORMALIZE
125             SN=SQRT(-H*DF)
126             DO 73 J = MA,MB
127      73     S(J) = S(J)/SN
128      C      ............PRINT SOLUTION
129             IF (NS.NE.1) GO TO 80
130             PRINT 204,KV,E
131             PRINT 205,(I,S(I),I=1,MB,IPSIQ)
132      80     E0=E
133             RETURN
134      83     PRINT 202,KERR
135             SCHR = 2
136             RETURN
137      201    FORMAT('1',' SCHR- SOLUTION OF RADIAL SCHR. EQUATION FOR V= ',I3,5
138             +X,'ETRIAL=',1PE15.7,'      (1/CM)'/
139             +' ITER,',5X,'E',14X,'F(F)',12X,'DF(E)',11X,'C(E)',4X)
140      202    FORMAT(' KERR = ',I2,' DIFF EQATION SOLUTION TECHNIQUE FAILT')
141      203    FORMAT(///I4,2X,1P4F16.7,5X,' THE CROSSING PT. OCCURS AT ',I4)
142      204    FORMAT('1 SCHR-SOLUTION OF RADIAL SCHR. EQUATION FOR V= ',I3,' E=
143             +',1PE15.7/'0   I',7X,'S(I)   ',5(20H    I          S(I)    ))
144      205    FORMAT(6(I5,1PE15.7))
145             END
```

```
1               SUBROUTINE PLLY'.
2               COMMON/TI/X(2403),Y(2400),NUMX,NPOLY,POLYU,XXX
3       C       THE ARRAY X HAS TO BE IN INCREASING ORDE
4               NM = (NPOLY+1)/2
5               NM1 = NM +1
6               NUP = NUMX + NM1 - NPOLY
7               DO 2 J = NM1,NUP
8               IF (XXX.LE.X(J)) GO TO 4
9       2       CONTINUE
10              J=NUP
11      4       L= J-NM
12              LLL=L + NPOLY -1
13              POLYN = 0.0
14              DO 6 K=L,LLL
15              TERM = 1.0
16              DO 5 M =L,LLL
17              IF (K.NE.M) TERM =TERM*(XXX-X(M))/(X(K)-X(M))
18      5       CONTINUE
19              TERM = Y(K)*TERM
20      6       POLYN=POLYN +TERM
21              RETURN
22              END
```

```
      SUBROUTINE HETRL(TX)
C     THIS SUBROUTINE CALCULATES THE VALUES OF ETRIAL AND B-RIAL. IF
C     NTRIAL=0 THE VALUES ARE TAKEN WHICH HAVE BEEN READ IN F? M THE
C     RK? DECK.
      DIMENSION YIA(10)
      COMMON/YD/YDM(20,10),IM(10)
      COMMON/AN4/ETRIAL(100),BTRIAL(100),AJTT,NTRIAL,KV(100)
      IF (NTRIAL.EQ.0) RETURN
      NC=0
      NIN=NTRIAL
      E0=0.
      DO 40 I = 1,NIN
      KV(I) = NC
      NC = NC +1
      ANV =FLOAT(I) - 0.5
      NAB = 0
      DO 10 IA = 1,10
      NGBD = IM(IA)
      IF (NGBD.EQ.0) GO TO 20
      NAB = NAB +1
      FACV = 1.
      YIA(IA)= 0.
      DO 10 IB = 1,NGBD
      YIA(IA) = YIA(IA) + FACV*YDM(IB,IA)
   10 FACV = FACV*ANV
   20 YIA(NAB+1)=0.
      ETRIAL(I)=0.
      BTRIAL(I)=0.
      FACJ=1.
      DO 30 IA = 1,NAB
      ETRIAL(I)=ETRIAL(I) + YIA(IA)*FACJ
      AIA=IA
      BTRIAL(I)= BTRIAL(I) + YIA(IA+1)*FACJ*AIA
   30 FACJ=FACJ*AJTT
      IF (ETRIAL(I).LT.E0) GO TO 50
      IF (ETRIAL(I).GT.TX) GO TO 50
   40 E0 = ETRIAL(I)
      GO TO 60
   50 NC=NC -1
   60 NTRIAL = NC
      RETURN
      END



      SUBROUTINE PLEGE(Z)
C     THIS SUBROUTINE CALCULATES THE LEGENDRE POLYNOMIALS YPL BY MEANS
C     OF A RECURSION RELATION AND MULTIPLIES THEM BY AN EXPONENTIAL CUT
C     OFF FUNCTION AS REQUIRED FOR THE CORRECTION FUNCTION WHICH M DI-
C     FIES THE POTENTIAL AFTER EVERY ITERATION.
      COMMON/PL/YPL(64),AA1,AA2,AA3,NPL
      ZZ= (Z-AA3)/(AA1+AA2*Z)
      YPL(1) = 1.
      YPL(2)=ZZ
      DO 10 I = 3,NPL
      AI = I
   10 YPL(I)= (YPL(I-1)*ZZ*(2.*AI-1.)-YPL(I-2)*(AI-1.))/AI
      FAC= ZZ**10*3.
      IF (FAC.GT.50.) GO TO 20
      FAC = EXP(-FAC)
      GO TO 30
   20 FAC=0.0
   30 DO 40 I=1,NPL
   40 YPL(I) =YPL(I)*FAC
      RETURN
      END
```

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```
  1            SUBROUTINE PCTTAB(GVT,AZERO,DE,M,NTRIAL)
  2        C   ROUTINE FOR INTERPOLATION OF INNER AND OUTER TURNING POINTS
  3            DIMENSION ZI(921)
  4            COMMON/PO/AINN(100),AOUT(100),EEE(100),BHB(100)
  5            COMMON/T1/XR(2403),YR(2403),NUMX,NPOLY,PCLYN,XXX
  6            COMMON/A2/V(2403)
  7            COMMON/A3/P(2403)
  8            COMMON/EX/XI(921),YI(921),N
  9            COMMON/TM1/AL(64,64),BL(64)
 10            COMMON/PL/YPL(64),AA1,AA2,AA3,NPL
 11        C   ...........SEARCH FOR MINIMUM
 12            DO 10 I = 1,M
 13     10     P(I) = P(I)+AZERO
 14            TX = V(1)
 15            DO 15 I = 2,M
 16            IF (V(I).GE.TX) GO TO 15
 17            TX=V(I)
 18            IMIN = I
 19     15     CONTINUE
 20        C   ...........INTERPOLATION OF THE POTENTIAL
 21            NPOLY = 4
 22            DO 30 NR = 1,2
 23            NA =1
 24            NB = IMIN
 25            IF (NR.EQ.1) GO TO 20
 26            NA=IMIN
 27            NB=M
 28     20     DO 25 I = NA,NB
 29            NUMX= I + 1 -NA
 30            K=I
 31            IF (NR.EQ.1) K = IMIN + 1 - I
 32            XR(NUMX)= V(K)
 33     25     YR(NUMX)=P(K)
 34            DO 30 I = 1,NTRIAL
 35            XXX=EEE(I)
 36            CALL PLLYNN
 37            IF (NR.EQ.1) AINN(I) = PCLYN
 38            IF (NR.EQ.2) AOUT(I) = POLYN
 39     30     CONTINUE
 40        C   ...........PRINTOUT OF THE TURNING POINTS
 41            PRINT 101
 42        C   PUNCH 101
 43            DO 35 I = 1,NTRIAL
 44            IA=I-1
 45            BBB(I)=BHB(I)+100.0
 46            IF (IA.EQ.40) PRINT 101
 47        C   PUNCH 102,IA,EEE(I),AINN(I),AOUT(I),BHB(I)
 48     35     PRINT 102,IA,EEE(I),AINN(I),AOUT(I),BBB(I)
 49            DO 40 I = 1,M
 50            XR(I) = P(I)
 51     40     YR(I)=V(I)
 52            NUMX =M
 53            IA = 0
 54            IB = N +1
 55            DO 55 I=1,N
```

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```
56                      XXX = XI(I)
57                      IF (XXX.GE.P(1)) GO TO 45
58                      IA = I
59                      GO TO 55
60            45        IF (XXX.LE.P(M)) GO TO 50
61                      IB = I
62                      GO TO 60
63            50        CALL PLLYNN
64                      ZI(I)= YI(I) - POLYN
65                      YI(I) = POLYN
66            55        CONTINUE
67            60        IF(IA.EQ.0) GO TO 70
68                      DO 65 I = 1, A
69                      ZI(I) = ZI(IA+1)
70            65        YI(I)=YI(I)-ZI(I)
71            70        IF (IB.EQ.(N+1)) GO TO 8C
72                      DO 75 I = IB,'
73                      ZI(I) =ZI(IB-1)
74            75        YI(I)=YI(I) -ZI(I)
75        C           .....PRINTOUT OF THE FINAL POTENTIAL AND OF THE STANDARD ERROR:
76            80        PRIN  103
77                      DO 99 I = 1,'
78                      ST = XI(I)/AZERO
79                      CALL PLEGEN(ST)
80                      ST=0.0
81        C             DO 85 K = 1,NPL
82        C 85        ST =ST + BL(K,1)*YPL(K)
83        C             IF (ABS(ST).GT.1.0D-6) GO TO 90
84        C             ST=0.0
85        C             GO TO 99
86        C 90        ST=0.0
87                      DO 95 J=1,NFL
88                      DO 95 K =1,NFL
89            95        ST = ST + YPL(K)*AL(K,J)*YPL(J)
90                      ST = SQRT(ABS(ST))*GVT
91            95        PRINT 104,XI(I),YI(I),ZI(I),ST
92            101       FORMAT(1H1,'   FINAL SET OF TURNING POINTS'//5X,1HV,3X,'L(M)',1:V
93            +,'RMIN',11X,'RMAX',15X,'BV*100'/)
94            102       FORMAT(1X,I5,F15.3,F14.6,F15.6,F15.7)
95            103       FORMAT(1H1,'   FINAL POTENTIAL'//12X,'P',1FX,'L(P)',13X,'K--:PA',1
96            +2X,'ERROR'/)
97            104       FORMAT (1X,1PD20.9,3D20.9)
98                      RETURN
99                      END
```

```
            POTENTIAL OF THE PHC      MOLECULE    (TOTAL FIT)
               GROUND STATE FOR LEAD OXIDE


   THE CODE NUMBER FOR THIS STATE IS


   HE MASSES OF THE TWO ATOMS,
    BASED ON C=12 ARE  1.5999400000D+01  AND   2.0715000000D+02


   DE =   .3157000D+05              TE =   C.
```

LIM1 = 1.0000 LIM2 = 7.5000 VFIN = 74.00 VINC = .25

IOPFG = 0 IPNRKR = 1 IPHIPA = 0

PCTENTIAL GENERATED BY RKR IS AS FOLLOWS

V	POTENTIAL ENERGY	INERTIAL ENERGY	FMIN	FMAX	RMIN. ACTION INTEGRAL	C
-.25	179.9606	.3064251300+00	1.836050991	1.367086 24	.327 951000-1	.177 007-1
0.00	359.5572	.3063406500+00	1.866776556	1.66(832 21	.7601? 95-1	.101 07-1
.25	538.7080	.3055342000+00	1.857032000	1.905944626	.3261 40-01	.174 674-1
.50	717.4136	.3054360500+00	1.847636774	2.00694452	.7077200-01	.214 645-1
.75	895.6741	.3050359300+00	2.036405742	2.01723400	.1712 41-1	.243 577 4-1
1.00	1073.4978	.3045639500+00	1.433245644	2.027014-25	.771401770-1	.2621 477-1
1.25	1250.8612	.3041300000+00	1.425661144	2.03712144	.1151901000-0	.343 34 727-1
1.50	1427.7884	.3036743500+00	1.410424122	2.04592243	.12117 724000	.3733 274-1
1.75	1604.2717	.30321673000+00	1.401401515	2.0042120043	.121777 1059-0	.3221 277-1
2.00	1780.3314	.3027257250+00	1.400770239	2.0002510+0	.12077063000	.3564 444-1
2.25	1955.5077	.3022290500+00	1.403035615	2.370063 85	.1347 675 009+0	.3721 14-1
2.50	2131.0609	.3018326500+00	1.709516054	2.07749441	.15 1025 09+0	.17 25 71-1
2.75	2305.7712	.3013674530+00	1.79473.403	2.06477447?	.144 273 40+0	.42177155-1
3.00	2480.0388	.3007005550+00	1.766017 54	2.091770057	.15047070700	.41620741-1
3.25	2653.8638	.3004316050+00	1.76479324	2.0646475-7	.156 015 90+00	.4217 74744-1
3.50	2827.2465	.2999609500+00	1.722616414	2.10526747	.1667715 0-00	.43225 05-1
3.75	3000.1771	.2990138500+00	1.775532 553	2.1053267040	.16514 1100+0	.4460 20 40-1
4.00	3172.6657	.2988700550+00	1.771883654	2.12470024.	.171524 5 09+0	.4677710-1
4.25	3344.7425	.2985374640+00	1.767555.74	2.130632774	.174012 115-0	.4577701-1
4.50	3516.3575	.2980592550+00	1.765337435	2.137046011	.141 0740 00+0	.4720 735-1
4.75	3647.5310	.2975791300+00	1.763000760	2.143097212	.145615 10000	.40672770-1
5.00	3858.2630	.2970971550+00	1.750111-06	2.1430072134	.1043734 39-0	.5042 1120-1
5.25	4028.5536	.2966132200+00	1.759190602	2.146055760	.1347237000	.5254 074-1
5.50	4198.4030	.2961275500+00	1.756266076	2.154936100	.19135 1170-0	.524 5901771-1
5.75	4367.8112	.2956399300+00	1.753410512	2.160744724	.20366010000	.5377660170-1
6.00	4536.7782	.2951504500+00	1.750645435	2.16649077	.2075724570000	.5420 3650-1
6.25	4705.3042	.2946590400+00	1.74754 421	2.172174150	.21211244700000	.55405-1
6.50	4873.3891	.2941658500+00	1.745321453	2.177 06034	.21 7235 009-00	.567077-1
6.75	5041.0330	.2936707300+00	1.742760 73	2.142272 31	.706 746371000	.35 74 65-1
7.00	5208.2359	.2931737500+00	1.740263341	2.184656 52	.2243167 50+00	.571 27750 0-1
7.25	5374.9979	.2926748400+00	1.737825746	2.1942771150	.222731170000	.5401661-1
7.50	5541.3184	.2921749550+00	1.735447420	2.160680 31	.72326702500+00	.60161640-1
7.75	5707.1987	.2916781550+00	1.733114622	2.20515775F	.2360 420000	.6176600770-1
8.00	5872.6376	.2911670500+00	1.730846000	2.21054000	.2345100 970000	.624 557 40-1
8.25	6037.6353	.2906666400+00	1.720622356	2.215066F1	.243620 6440-0	.626 5571-1
8.50	6202.1420	.2901524500+00	1.726466607	2.221047 54	.247350629000	.645 121 740-1
8.75	6366.3074	.2896423310+00	1.724316044	2.227673729	.2510902270000	.654 174 770-1
9.00	6529.9815	.2891303560+00	1.722231201	2.231616037	.75463747000	.666760 170-1

9.25	6693.2192	.2886169E-0+C0	1.7201F 253	2.2367F640F	
9.50	6856.0654	.2881007560+C0	1.71P1P619h	2.241EF4??	
9.75	7012.3550	.2875h313.0+0C	1.71622365E	3.24710E 55	
10.00	7180.2628	.2h7C6365.0+00	1.7142962555	2.2E222610?	
10.25	7341.728?	.2865422F+0+C0	1.712411702	2.2E7710E64	
10.50	7502.7527	.2h601905C0+00	1.710559744	2.2623776C07	
10.75	7663.3345	.2855?9393.0+00	1.7687421F67	2.2724576?.	
11.00	7823.473P	.2849E6651.0+C0	1.7C6955 361	2.2724 764.	
11.25	7983.1706	.2844380P 0+00	1.7C5205?6?	2.27746 101	
11.50	8142.4246	.2P35-3735E0+00	1.7034665657	2.2F746F15	
11.75	8301.2357	.2833?473.0+0?	1.7017969467?	2.2F7442C07	
12.00	8452.6035	.2824902560+0L	1.700136 42	2.2634956?4	
12.25	8617.5279	.2h23C3A?. C+00	1.6969C2e452	2.2E7354F17	
12.50	8775.0086	.2817656.5C0+CC	1.6953265565	2.3C22C64	
12.75	8932.C453	.2H122553.0+CC	1.6937772521	2.3F7214F1?	
13.00	90?8.637?	.2866.555.C+C0	1.6922253.54	2.312126 1	
13.25	9244.7?5?	.2801396?-0+C0		2.317CCF604	

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THE DUNHAM COEFFICIENTS

POTENTIAL OF THE FEO   MOLECULE   (TOTAL FIT)
GROUND STATE FOR LEAD OXIDE

FIT OF INNERPOST TURNING POINTS FOR EXTRAPOLATING U(R) WITH A LESS THAN ...

FUNCTION OF THE FORM   EXP(C(1)+B(2)*X+E(3)*X*X+...+B(K)*X*...*(K-1)) ...

R	LOG(L(R))	FCALC	DIFF

CONSTANTS OF FIT

EC 2) = .61259577C-C1   RMS ERROR= .37057/5470-C..   RELATIVE RMS ERROR = ...

LRDER OF ENTRIES : 4 STANDARD ERROR = 2.02171D-05

FIT OF OLTERMOST PLAINING POINTS FOR EXTRAPOLATING LOAD WITH N GREATER THAN 4.652 CAT-.. U-TNC

FRACTION OF THE FORM B(1)+E(2)+..+C-(E)+H(3)+R+..+H(K)+..+(TH N=M(C)... 4

R	L(R)	FCALC	C EE	RELATIVE RMS ERROR
4.8652R0409C+C0	3.15174376CC+C4	3.15174376490+C4	1.0731263CC30+C7	.74,649798C-C4
4.8C2524C5CC+C0	3.15C70661D0+C4	3.15C70644000+C4	-2.224624525F-C7	.7CC9-1571F-C7
4.7454137C1C+C0	3.14558217C0+C4	3.14C6C2253D+04	-3.7EC-4151C0-C4	.41CC22270C-
4.6620261E1C+00	3.1983704140C+C4	3.14L37072400+C4	1.6C2C222C4F-C7	.1245124CCC4C0
4.64222564CC+00	3.14707254C1C+C4	3.147C727590+C4	1.4157508FC-C7	
4.555C2532PC+C0	3.14568497C1C+C4	3.1456E67720+C4	-6.415CCCC00C-C4	
4.45NEEC3440C+C0	3.14421e5C0C+C4	3.14421P7130+C4	-2.12672760C0-C3	
4.51C019663C+C0	3.14266264CC+C4	3.14266255150+C4	1.2CC7337CC5F-C3	

CONSTANTS OF FIT

EC 1) =	.21598349E1C+05	RMS ERRCR=	.F4726173H50+00
EC 2) =	.251E50259C+C7	RMS ERRCR=	.H9096r232C+05
EC 3) =	-.7CC495122C+CA	RMS ERRCR=	.202C59255C+07
EC 4) =	-.204783164C+C9	RMS ERRCR=	.2544EE1404C+0F

LRDER OF ENTRIES : A STANDARD ERROR = 2.0F1200-C3

BEGINNING OF INVERTED PERTURBATION APPPCACH

RMIN = 1.400, RAMAX = 7.500, SPACING = .CCCC1000
CONVERGENCE CRITERICA IS ERRCH LESS THAN .10C-02

ALRDER OF ITERATIONS = 4

PARAMETERS OF THE FITTING POLYNOMIAL

RMIN = 1.595RMAX = 4.115 RE = 1.522 ,NPL= 1C

N	GU CAL	EU MEAS	GU P-C	EU CAL	EV P-C	S(MA)	C(BE)	MB	AB

B(1) = -1.032018460+02   RMS ERROR =   1.3290040+03   RELATIVE RMS ERROR =   1.0 71E+01
B(2) = -2.326206235+02   RMS ERROR =   2.054670+03   RELATIVE RMS ERROR =   1.0 17E+01
B(3) = -1.270041920+02   RMS ERROR =   2.341410+01   RELATIVE RMS ERROR =   1.7 45E+01
B(4) = -3.179065807+01   RMS ERROR =   6.510420+02   RELATIVE RMS ERROR =   2.1155E+01
B(5) = -4.252265400+01   RMS ERROR =   1.152620+03   RELATIVE RMS ERROR =   6.14 75E+01
B(7) = -1.075305455+02   RMS ERROR =   1.542767+03   RELATIVE RMS ERROR =   7.1 741E+01
B(8) = 1.757475550+01   RMS ERROR =   6.124170+02   RELATIVE RMS ERROR =   1.0 71E+01
B(9) = -2.846576069+01   RMS ERROR =   3.269116+02   RELATIVE RMS ERROR =   9.1 743E+01
B(10) = 2.804516122+01   RMS ERROR =   1.262784+02   RELATIVE RMS ERROR =   4.0 27E+01

RESULTS OF SCHROEDINGER EQUATION FOR J(J+1) =   2. AND J= 1

RESULTS OF SCHROEDINGER EQUATION FOR J(J+1) = 0. AND J= 0

#	EV CAL	EV MEAS	QV P-C	EV CAL	EV M-C	S(PA)	S(PA)	MA	NE
0	359.10303	359.14042	.03739						
1	1072.10090	1072.07310	-.02731						
2	1779.93394	1775.89466	-.03531						
3	2479.64714	2479.62200	-.02514						
4	3172.27271	3172.26796	-.00377						
5	3857.83223	3857.84624	.01461						
6	4536.33816	4536.36144	.02332						
7	5207.79575	5207.81120	.01630						
8	5872.20453	5872.22043	.01630						
9	6525.55761	6529.56471	.00510						
10	7179.85277	7175.64608	-.06670						
11	7823.07320	7823.05708	-.01612						
12	8459.20199	8459.18677	-.02122						
13	9086.24235	9086.22109	-.02126						
14	9710.15959	9710.14291	-.01668						
15	10324.94069	10324.93198	-.00871						
16	10932.56426	10932.56497	.00041						
17	11533.00618	11533.01545	.00026						
18	12126.23443	12126.25288	.01545						
19	12712.22569	12712.24765	.01747						
20	13290.94467	13290.96104	.01637						
21	13862.34414	13862.35521	.01102						
22	14426.38501	14426.38430	.00323						
23	14983.02684	14983.01526	-.00556						
24	15532.20157	15532.18P00	-.01357						
25	16073.87446	16073.85532	-.01914						
26	16607.93407	16607.96292	-.02116						
27	17134.07251	17134.45341	-.01410						
28	17653.27653	17653.26631	-.01323						
29	18164.30247	18164.33603	-.00444						
30	18667.59610	18667.60149	.00575						
31	19162.97235	19162.9P.11	.01676						
32	19650.40004	19650.42384	.02560						
33	20129.60457	20129.63209	.02751						
34	20631.10780	20601.13640	.02401						
35	21064.22782	21064.25243	.02492						

COEFFICIENTS OF THE LEGENDRE POLYNOMIALS AFTER ITERATION NO. 3

SUM OF DIFF.= 0.   AVERAGE CIFF. = 0.   RMS CF EV = 0.

BC(1) =	1.436915501D+01	RMS ERRCH =	5.075464C0D+01	RELATIVE RMS ERRCP =
BC(2) =	-3.367386970D+01	RMS ERRCH =	2.07PF090D+02	RELATIVE RMS ERRCL =
BC(3) =	3.711769023D+01	RMS ERRCH =	1.554313D+02	RELATIVE RMS ERRCL =
BC(4) =	-2.808849202D+01	RMS ERRCH =	5.24369ED+01	RELATIVE RMS ERRCP =
BC(5) =	2.652593500D+01	RMS ERRCH =	6.52839FD+01	RELATIVE RMS ERRCF =
BC(6) =	-1.H7437537ED+01	RMS ERRCH =	1.C1CC56D+C2	RELATIVE RMS ERRCF =
BC(7) =	8.732476393D+00	RMS ERRCH =	5.39C790D+01	RELATIVE RMS ERRCP =
BC(8) =	-6.754872896D+00	RMS ERRCH =	1.85F436D+C1	RELATIVE RMS ERRCP =
BC(9) =	5.157796552D+00	RMS ERRCI =	1.7593A0C+01	RELATIVE RMS ERRCP =
B(10) =	-1.493355509D+00	RMS ERRCH =	8.664335D+0C	RELATIVE RMS ERRCP =

CORREL. TICK MATRIX OF THE COEFFICIENTS

1	1.000000									
2	.999991	1.000000								
3	.993053	.999222	1.000000							
4	.966466	.967902	.97042	1.000000						
5	.972274	.952756	.9 6420	.96 741	1.00000					
6	.998493	.998437	.956833	.561515	.6 1033	1.00000				
7	.997258	.997245	.946017	.763434	.561305	.99 70	1.00000			
8	.988955	.989452	.993116	.567154	.6 8617	.99 547	.9 62	1.00000		
9	.956893	.996810	.954951	.956526	.969489	.969513	.5 717	.	1.0	
10	.976161	.975594	.968629	.907182	.957251	.946251	.565752	.563 32	.5 51	1.

FINAL SET CF TURNING PCINTS

N	U(R)	RMIN	RMAX	BV-1JC
0	359.103	1.875111	1.9c7533	30.4276568
1	1073.101	1.63b644	2.034213	30.2637328
2	1779.934	1.614851	2.0c8430	30.0551 72
3	2475.647	1.796367	2.0c7640	29.221527
4	3172.273	1.780940	2.124004	29.7447207
5	3857.832	1.767616	2.14c50c	29.56302-0
6	4536.338	1.755847	2.171701	29.377205
7	5207.796	1.745269	2.153925	29.1873730
8	5972.205	1.735712	2.215411	28.4936413
9	6629.560	1.726953	2.236325	28.7561079
10	7179.853	1.718691	2.256789	28.5944556
11	7823.073	1.711432	2.276899	28.3891536
12	8459.208	1.704505	2.296730	28.1614551
13	9088.242	1.698050	2.316345	27.9664234
14	9710.160	1.692021	2.335793	27.7536930
15	10324.941	1.686379	2.355120	27.5349157
16	10932.564	1.681050	2.374361	27.3125457
17	11533.006	1.676126	2.393550	27.086-434
18	12126.238	1.671464	2.412716	26.3578 02
19	12712.230	1.667002	2.431686	26.6257366
20	13290.945	1.662960	2.451093	26.3504995
21	13862.344	1.659081	2.47032c	26.1522617
22	14426.385	1.655429	2.489646	25.9111142
23	14983.021	1.651569	2.509052	25.6671456
24	15532.202	1.648745	2.528567	25.4204370
25	16073.874	1.645654	2.548208	25.1710620
26	16607.984	1.642814	2.567992	24.9190 33
27	17134.473	1.640058	2.587939	24.6645545
28	17653.280	1.637537	2.606063	24.4075431
29	18164.342	1.635121	2.628384	24.1480 73
30	18667.596	1.632845	2.648517	23.6862447
31	19162.572	1.630701	2.66966e2	23.6220 01
32	19650.400	1.628682	2.690656	23.3556 10
33	20129.805	1.626788	2.711976	23.0670596
34	20601.108	1.625012	2.733548	22. 164303
35	21064.228	1.623349	2.755925	22.543756
36	21519.079	1.621801	2.777631	22.26c1622
37	21965.572	1.620365	2.800189	21.9527177
38	22403.614	1.619046	2.823121	21.7144 35
39	22833.108	1.617843	2.846454	21.4344-83

FINAL SET CF TURNING PCINTS

V	U(R)	RPIN	RPAX	BV-17C
40	23253.556	1.616741	2.670214	21.1527765
41	23666.054	1.615732	2.807443!	20.8693027
42	24069.298	1.614612	2.919135	20.5940289
43	24463.581	1.613973	2.544361	20.2967770
44	24848.791	1.613735	2.970146	20.2077916
45	25224.818	1.614496	2.948632	19.7164351
46	25591.545	1.615416	3.003561	19.4227953
47	25948.855	1.616414	3.051265	19.1265642
48	26296.628	1.617435	3.079755	18.4275256
49	26634.741	1.618407	3.109041	18.5253222
50	26963.067	1.619267	3.135202	18.2196127
51	27281.476	1.620034	3.170317	17.9100053
52	27589.834	1.620616	3.202471	17.5360655
53	27888.005	1.621013	3.235762	17.2773006
54	28175.645	1.621198	3.270295	16.9532547
55	28453.210	1.621171	3.306207	16.6231714
56	28719.950	1.620524	3.343628	16.2865724
57	28975.911	1.620460	3.382727	15.9542/130
58	29220.534	1.619766	3.423693	15.596 332
59	29454.659	1.618914	3.466746	15.2301060
60	29677.523	1.617862	3.512145	14.8556250
61	29888.759	1.616649	3.560192	14.474040
62	30088.402	1.615299	3.611250	14.0453424
63	30276.286	1.613837	3.665752	13.6792231
64	30452.248	1.612293	3.724226	13.2596732
65	30616.126	1.610695	3.717324	12.6220 70
66	30767.763	1.609074	3.855863	12.3675931
67	30907.005	1.607461	3.930893	11.492705
68	31033.701	1.617871	4.013794	11.3645030
69	31147.698	1.619633	4.166466	10.6662172

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FINAL POTENTIAL

R	U(R)	PKE-IPA	FORCE
1.4090000000D+00	3.1865015200+04	4.1675115830-01	C.
1.4072131830+00	3.1647577660+04	4.1675115900-31	C.
1.4144265660D+00	3.1630146370+C4	4.1675115760-01	.
1.4216395480+00	3.1612723820+04	4.1675115610-01	.
1.4288527310+00	3.1795311100+C4	4.1675115910-01	.
1.4360659140+00	3.1777907520+04	4.1675115670-01	.
1.4432790970+00	3.1760514260+C4	4.1675115970-01	.
1.4504922790+00	3.1743130130+C4	4.1675115950-01	..
1.4577054620+00	3.1725755500+34	4.1675115710-01	0.
1.4649186450+00	3.1708350390+04	4.1675115740-01	C.
1.4721318280+00	3.1691030780+04	4.1675115840-01	C.
1.4793450100+00	3.1673688680+04	4.1675115770-01	J.
1.4865581930+00	3.1656352060+C4	4.1675115400-01	..
1.4937713760+00	3.1639024940+04	4.1675115740-01	C.
1.5009845590+00	3.1621707300+C4	4.1675115760-01	C.
1.5081977410+00	3.1604399140+04	4.1675115940-01	C.
1.5154105240+00	3.1587100450+04	4.1675115950-01	0.
1.5226241070+00	3.1569811230+C4	4.1675115650-01	C.
1.5298372960+00	3.1552531470+C4.	4.1675115760-01	C.
1.5370504720+00	3.1535267230+04	4.1069432860-01	C.
1.5442636550+00	3.1517849180+C4	-4.1055395860-01	1.2024807460-19
1.5494635930+00	3.1506311100+34	7.5437033940-C1	2.5574455960-11
1.5541235620+00	3.1495444870+C4	3.7729465240-01	2.5064757620-0.
1.5583231920+00	3.1482296710+04	4.1213559960-01	3.55755556000-06
1.5621275940+00	3.1470314040+C4	4.1536626520-01	1.4163425 10-04
1.5655859600+00	3.1456424010+C4	4.5566049960-01	2.0322860450-07
1.5687519480+00	3.1441748060+04	4.3654515840-01	1.5354674660-02
1.5716495230+00	3.1426553470+C4	7.2524557310-02	7.31-412C6960-03
1.5743123710+00	3.1411163060+04	-5.656497010-01	2.4449425470-01
1.5767656540+00	3.1397243610+C4	-4.2514193470+0.	6.5785634450-C1
1.5790311420+00	3.1384770240+04	-9.9273506510+00	1.4363206070+0.
1.5811271640+00	3.1375034910+04	-1.9145236361D+01	2.70 526201 0+0.
1.5830699060+00	3.1368503680+04	-3.2405162310+01	4.55E5F4 FE0+0.
1.5448733680+00	3.1366465930+04	-5.1002240590+01	7.0065526330+C.
1.5865458780+00	3.1366834960+04	-7.2837703640+C1	1.0070495450+C1
1.5881103020+00	3.1369033660+C4	-5.7334552370+01	1.3556164060+C1
1.5895643040+00	3.1373655670+04	-1.2506312430+02	1.7453716360+C1
1.5909203720+00	3.1380963230+C4	-1.5634270120+02	2.1730204560+01
1.5921862940+C0	3.1387736320+C4	-1.8789219780+02	2.6162491510+C1
1.5933688600+00	3.1393309580+C4	-2.1905723970+02	3.065275824C+01
1.5944743280+00	3.1397270660+04	-2.4942845990+02	3.5241053740+01
1.5955082850+00	3.1401612040+C4	-2.8099331650+02	3.9736072060+01
1.5964759010+00	3.1408356250+04	-3.1590053562D+02	4.4125262540+01
1.5973815770+00	3.1411636850+04	-3.4769531602D+02	4.8366552670+C1
1.5982297580+00	3.1410916050+C4	-3.7681179429D+02	5.2436373060+C1
1.5990242650+00	3.1406063620+04	-4.0243274760+02	5.6315225760+C1
1.5997685990+00	3.1397203500+04	-4.2479794660+02	5.9578513950+C1
1.6004660390+00	3.1384461200+C4	-4.4411672160+02	6.3453676800+31
1.6011195580+00	3.1368216640+04	-4.6068786750+02	6.6710615420+C1
1.6017319720+00	3.1407444070+04	-5.3353673060+02	6.9763071540+C1
1.6023058000+00	3.1460102540+04	-6.2060546260+02	7.2616291110C+C3
1.6028434180+C0	3.1459113510+04	-6.9451062320+02	7.5235525560+C1
1.6035347C030+00	3.1523270220+C4	-7.5454259710+02	7.7757875420+C1
1.6038146640D+00	3.1532298500+04	-8.0072433490+02	7.9005152340C+C1
1.6042602460+00	3.1526557060+34	-5.3254171960+02	C.2211852940+C1
1.6046735680+0C	3.1566996140+C4	-8.5124612730+02	8.4257525360+C1
1.6050602670+00	3.1474670210+34	-8.5759728970+02	8.6345767070+C1
1.6054215060+00	3.1430976430+C4	-8.5414132640+02	8.7761592060+C1
1.6057595340+00	3.1377356260+C4	-8.4112322690+02	8.9346301660+C1
. ...+00	3.		.

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1.6163705560+00	3.1246216420+04	-7.7346+3.640+02	9.2176+7.2.9+01
1.6096645470+00	3.1171547360+04	-7.6167670590+02	9.34341576.0+01
1.6069021060+00	3.1092602420+04	-7.2636233710+02	9.4556669660+01
1.6071410150+00	3.1010599070+04	-6.4473569450+02	6.5670695920+01
1.6073633870+00	3.0926645210+04	-6.4951819430+02	9.6663393040+01
1.6075701630+00	3.0772830560+04	-5.4157251240+02	9.7576356230+01
1.6077622730+00	3.0610464410+04	-4.2622152130+02	9.4422651650+01
1.6079405340+00	3.0455165170+04	-3.1625653950+02	9.9271067560+01
1.6081057660+00	3.0307495850+04	-2.1855913.0+02	9.5911723720+01
1.6082587480+00	3.0167701560+04	-1.2773026650+02	1.0057711.050+02
1.6084001520+00	3.0035597470+04	-4.5556523850+01	1.0116336560+02
1.6085307800+00	2.9912341260+04	2.7748191540+01	1.0172366170+02
1.6086511970+00	2.5796711140+04	9.2406653620+01	1.0235065350+02
1.6087620260+00	2.5669963120+04	1.4941517340+02	1.0271945620+02
1.6088635000+00	2.9568874300+04	1.9604636290+02	1.0314644430+02
1.6089573730+00	2.9496162090+04	2.2557026450+02	1.0353763470+02
1.6090429660+00	2.9410611410+04	2.6725051370+02	1.0315444350+02
1.6091212220+00	2.9331824730+04	2.9143442200+02	1.0421952440+02
1.6091922010+00	2.9255514720+04	3.0643066900+02	1.0451506870+02
1.6092575860+00	2.9192326040+04	3.1659454670+02	1.0478327230+02
1.6093166260+00	2.9132916310+04	3.2227956490+02	1.0532644550+02
1.6093701710+00	2.9077900450+04	3.1986552800+02	1.0524635020+02
1.6094185970+00	2.9027964940+04	3.1167033710+02	1.0544472350+02
1.6094623260+00	2.8982730880+04	2.9607566240+02	1.0562355560+02
1.6095016950+00	2.8941894720+04	2.7938765860+02	1.0577842760+02
1.6095371170+00	2.8905063400+04	2.5600177620+02	1.0592662440+02
1.6095688950+00	2.8871947240+04	2.2821020550+02	1.0605793150+02
1.6095973980+00	2.8842196860+04	1.9636476130+02	1.0617372300+02
1.6096229150+00	2.8815516170+04	1.6876296400+02	1.0627727C 5+02
1.6096457820+00	2.8791570C8-C04	1.2174454710+02	1.0636596750+02
1.6096662690+00	2.8770091950+04	7.9577926000+01	1.0645252940+02
1.6096846790+00	2.8750763350+04	3.4576637450+01	1.0652741340+02
1.6097012730+00	2.8733334660+04	-1.2556626510+01	1.0655449570+02
1.6097163240+00	2.8717506520+04	-6.2834466720+01	1.0665530460+02
1.6097300820+00	2.8703027110+04	-1.1469951450+02	1.0671086560+02
1.6097427910+00	2.8689643430+04	-1.6739296060-D+02	1.0676212340+02
1.6097546870+00	2.8677106660+04	-2.2347320350+02	1.0681002350+02
1.6097660120+00	2.8665164310+04	-2.7957545370+02	1.0685573450+02
1.6097769670+00	2.8653605310+04	-3.3732259300+02	1.0695566260+02
1.6097877730+00	2.8642196810+04	-3.9558066340+02	1.0654336530+02
1.6097986520+00	2.8630705070+04	-4.5441241530+02	1.0656714650+02
1.6098057760+00	2.8618947560+04	-5.1363345010+02	1.0701316660+02
1.6098213490+00	2.8606707770+04	-5.7362499450+02	1.0707641420+02
1.6098335590+00	2.8593787370+04	-6.3238643610+02	1.0712747020+02
1.6098465950+00	2.8579984440+04	-6.9151363310+02	1.0717941310+02
1.6098606090+00	2.8565134750+04	-7.5024010510+02	1.0723605250+02
1.6098757920+00	2.8549036220+04	-8.0836157530+02	1.0726563650+02
1.6098923000+00	2.8531518180+04	-8.6657051540+02	1.0736305450+02
1.6099103030+00	2.8512396780+04	-9.2208677950+02	1.0742517370+02
1.6099259330+00	2.8491532410+04	-9.7735667640+02	1.0751370240+02
1.6099513630+00	2.8468731570+04	-1.0313311590+03	1.0755934560+02
1.6099747330+00	2.8443841870+04	-1.0636476650+03	1.0766265050+02
1.6100001790+00	2.8416711800+04	-1.1347545960+03	1.0775412220+02
1.6100278440+00	2.8387176640+04	-1.1638650290+03	1.0760433650+02
1.6100573700+00	2.8355091450+04	-1.2510915210+03	1.0702373730+02
1.6100903760+00	2.8320307450+04	-1.2762243860+03	1.0761526353+02
1.6101254930+00	2.8282673370+04	-1.3151350430+03	1.0735520716+02
1.6101633420+00	2.8242066320+04	-1.3556603509	1.0644186540+02
1.6102040630+00	2.8198305890+04	-1.3977015540+03	1.0660277560+02
1.6102477530+00	2.8151294070+04	-1.43307622'0+03	1.0877504140+02
1.6102945400+00	2.8100668650+04	-1.4656602120+03	1.0606411560+02
1.6103445340+00	2.8046905420+04	-1.4653167430+03	1.0615534720+02
1.6103976430+00	2.7962527150+04	-1.5215171320+03	1.0676400660+02
1.6104545200+00	2.7927851650+04	-1.5453234750+03	1.0656566510+02
1.6105144400+00	2.7662516160+04	-1.5654357540+03	1.0652023570+02

1.6106463660+00	2.7719411540+04	-1.5532246350+03	1.1042543210+00
1.6107173390+06	2.7641-13620+04	-1.6546775370+33	1.1310550340+00
1.6107932290+00	2.7559660240+04	-1.6103712930+03	1.1359531+10+00
1.6108726540+00	2.7472032780+04	-1.6121659580+03	1.1119504090+00
1.6109561470+00	2.7361357280+04	-1.6100474160+03	1.1151737010+00
1.6110493940+00	2.7266603C560+04	-1.6033498460+03	1.1195031540+00
1.6111355990+00	2.7185452210+04	-1.5935309640+03	1.1215755 370+00
1.6112324320+00	2.7094016750+04	-1.5770154060+03	1.1256041540+00
1.6113333420+00	2.6970020350+04	-1.5602614450+03	1.1292771020+00
1.6114368270+00	2.6854983460+04	-1.5372036560+03	1.1332956650+00
1.6115487470+00	2.6735055090+04	-1.5066402350+03	1.1373716750+00
1.6116637980+00	2.6610223160+04	-1.4761402230+03	1.1419529560+00
1.6117834660+00	2.6490482070+04	-1.4421291750+03	1.1475635780+00
1.6119080190+00	2.6345877070+04	-1.4011235430+03	1.1504425600+00
1.6120375400+00	2.6206453260+04	-1.3572605970+03	1.1551491 40+00
1.6121720116+00	2.6062239450+04	-1.3045644690+03	1.1555626350+00
1.6123116150+00	2.5913495280+04	-1.2557997910+03	1.1645213150+00
1.6124567200+00	2.5760201510+04	-1.1990042960+03	1.1700237040+00
1.6126065060+00	2.5602572970+04	-1.1306130570+03	1.1752679670+00
1.6127624390+00	2.5440824560+04	-1.0745943240+03	1.1806651271+00
1.6129234050+00	2.5275192000+04	-1.0072550320+03	1.1861719620+00
1.6130858740+00	2.5105591680+04	-9.3650176160+02	1.1918266250+00
1.6132619150+00	2.4932536050+04	-8.6361341700+02	1.1976125090+00
1.6134396020+00	2.4758227930+04	-7.8652619150+02	1.2035260590+00
1.6136230100+00	2.4622618200+04	-7.5345150840+02	1.2095637934+02
1.6138122060+00	2.4507535770+04	-7.3945451710+02	1.2157216070+00
1.6140072620+00	2.4392485860+04	-7.2605277370+02	1.2215596260+00
1.6142082520+00	2.4277652220+04	-7.1341636760+02	1.2283605550+00
1.6144152390+00	2.4163220370+04	-7.0173322160+02	1.2348726040+00
1.6146282950+00	2.4045367210+04	-6.9117856240+02	1.2414661190+00
1.6148474920+00	2.3932621300+04	-6.8191934450+02	1.2481556650+00
1.6150728970+00	2.3824066060+04	-6.7411173610+02	1.2549357500+00
1.6153045720+00	2.3712936880+04	-6.6796264260+02	1.2618003250+00
1.6155425940+00	2.3603010840+04	-6.6348621370+02	1.2687434460+00
1.6157870320+00	2.3494413310+04	-6.6050661520+02	1.2757586650+00
1.6160375520+00	2.3387255380+04	-6.6031405820+02	1.2828394650+00
1.6162954230+00	2.3281621210+04	-6.6179647230+02	1.2899796350+00
1.6165595100+00	2.3177600640+04	-6.6540770050+02	1.2971717650+00
1.6168302870+00	2.3075232010+04	-6.7120857950+02	1.3044071660+00
1.6171107810+00	2.2974525660+04	-6.7921593660+02	1.3116602350+00
1.6173592160+00	2.2875488680+04	-6.8941744130+02	1.3189631660+00
1.6176834080+00	2.2778070460+04	-7.0177270150+02	1.3262606130+00
1.6179816170+00	2.2682196080+04	-7.1620163630+02	1.3332647242+00
1.6182868420+00	2.2587757520+04	-7.3255472420+02	1.3405925070+00
1.6185991740+00	2.2494591290+04	-7.5076695450+02	1.3483364670+00
1.6189186690+00	2.2402498410+04	-7.7057792650+02	1.3555707670+00
1.6192454030+00	2.2311224420+04	-7.9171177610+02	1.3625876310+00
1.6195754450+00	2.2220462630+04	-8.1368035370+02	1.3710279050+00
1.6199203600+00	2.2106706750+04	-8.1357606650+02	1.3775366050+00
1.6202637220+00	2.1951095890+04	-8.1194055430+02	1.3847532630+00
1.6206261090+00	2.1875167250+04	-8.1049767560+02	1.3915206450+00
1.6209900780+00	2.1758947070+04	-8.0929024650+02	1.3990631030+00
1.6213617160+00	2.1642464120+04	-8.0832383980+02	1.4060771130+00
1.6217410440+00	2.1525744160+04	-8.0764072200+02	1.4130512170+00
1.6221282650+00	2.1408798520+04	-8.0724495990+02	1.4195465610+00
1.6225233310+00	2.1291635670+04	-8.0714371230+02	1.4261554240+00
1.6229263500+00	2.1174255460+04	-8.0733550440+02	1.4334725630+00
1.6233374080+00	2.1056644730+04	-8.0780560840+02	1.4400502410+00
1.6237565760+00	2.0938783420+04	-8.0853356140+02	1.4466027160+00
1.6241835240+00	2.0820640510+04	-8.0946822800+02	1.4533004155+00
1.6246195280+00	2.0702173370+04	-8.1061967630+02	1.4592650410+00
1.6250635010+00	2.0583320510+04	-8.1167209750+02	1.4654525440+00
1.6255155430+00	2.0464315880+04	-8.1317524600+02	1.4714857230+00
1.6259767660+00	2.0342002010+04	-8.1227055030+02	1.4773503650+00
1.6264462430+00	2.0217910290+04	-8.0978517050+02	1.4771655450+00

1.6279112790+00	1.99627913900+04	-4.0043134395030+02	1.44742700104044
1.6275070070+00	1.96420946900+04	-9.01749001900+02	1.45764975200+03
1.6224116550+00	1.97156134000+04	-7.98012464600+02	1.55045912430+03
1.62-9253340+00	1.95-461356000+04	-7.96007364400+02	1.50595-86510+03
1.6254480950+00	1.94610566900+04	-7.53640049500+02	1.51481791300+03
1.6299800590+00	1.93329431210+04	-7.303017-340+02	1.51957730300+03
1.6303521300D+00	1.92042544530+04	-7.46587597200+02	1.52417372650+03
1.6310713170+00	1.907456H4060+04	-7.43642658300+02	1.52047210+03
1.631632013D+00	1.89451203400+04	-7.90365560400+02	1.53255939370+03
1.6322016700+00	1.86139513130+04	-7.76241953600+02	1.53712276070+03
1.6327809990+00	1.86618771170+04	-7.716865137D+02	1.54113524400+03
1.6337300960+00	1.85491775680+04	-7.66528770640+02	1.54501039000+03
1.6339690520+00	1.84159277550+04	-7.62194491300+02	1.54073 7450+03
1.6345779830+00	1.82615994760+04	-7.57391732900+02	1.55222452700+03
1.6351970020+00	1.81471512350+04	-7.52272136100+02	1.555772025000+03
1.6358261950+00	1.80124675950+04	-7.47172360010+02	1.55500-30510+03
1.6364657040+00	1.78769531170+04	-7.41363007200+02	1.56226236100+03
1.6371150600+00	1.77406743900+04	-7.367095920+02	1.56531070700+03
1.6377776C300+00	1.76039276500+04	-7.313471276D+02	1.56-232122D+03
1.6384470970+00	1.74663097800+04	-7.25591073400+02	1.571025913D+03
1.6391289210+00	1.73280576800+04	-7.15678010400+02	1.57370736 D+03
1.6398216320+00	1.71892540000+04	-7.13689424200+02	1.57626792500+03
1.6405253370+00	1.70495161300+04	-7.076417P840+02	1.57-71460700+03
1.6412401330+00	1.69100520D+04	-7.015427+P600+02	1.58105513640+03
1.6419662940+00	1.67696754200+04	-6.95403352100+02	1.58320075100+03
1.6427037910+00	1.66287943600+04	-6.69232576200+02	1.56540558 D+03
1.6434528310+00	1.64847411490+04	-6.63031552290+02	1.56743001550+03
1.6442135400+00	1.63454833800+04	-6.76756F09640+02	1.5P-35549600+03
1.6449860640+00	1.62029362600+04	-6.70231565+0400	1.57116467100+03
1.6457705470+00	1.60559097900+04	-6.63866645F0+02	1.55325240F00+03
1.6465671440+00	1.59164152000+04	-6.574625373D+02	1.55456395900+03
1.6473760060+00	1.57724667E0+04	-6.51347617D+02	1.59611722000+03
1.6491972980+00	1.56280719700+04	-6.446395900400+02	1.59756141000+03
1.6490311600+00	1.54633237510+04	-6.3426533100+02	1.59855575240+03
1.6498777130+00	1.53337976510+04	-6.31423603000+02	1.600124610700+03
1.6597373150+00	1.51921945900+04	-6.25536649500+02	1.601447391000+03
1.6516095510+00	1.50455967970+04	-6.19162624100+02	1.6025611530+03
1.6524956620+00	1.48993252900+04	-6.123400944U+02	1.60356643950+03
1.6533552320+00	1.47522867750+04	-6.06576353000+02	1.6094522465D+03
1.6543042530+00	1.46046949830+04	-6.00377777040+02	1.60553696210+03
1.6552351170+00	1.44570212900+04	-5.94249309200+02	1.60612294000+03
1.6561760310+00	1.43088037400+04	-5.68191 9210+02	1.60672906660+03
1.6571311960+00	1.41601241800+04	-5.62131665410+02	1.60734556100+03
1.6591003220+00	1.40110622590+04	-5.761484509O+02	1.6078620760+03
1.6590851420+00	1.38616263700+04	-5.70248577700+02	1.60816727+C+03
1.6600843690+00	1.37118225400+04	-5.64434512100+02	1.6064419446D+03
1.6610987420+00	1.35616530400+04	-5.58719543900+02	1.60855057270+02
1.6621294920+00	1.34111155300+04	-5.53093123000+02	1.6005561230+03
1.6631738850+00	1.32601670000+04	-5.475025942D+02	1.60P45915210+03
1.6642351600+00	1.31088416ED+04	-5.41554062900+02	1.60627171700+03
1.6653125940+00	1.29571569000+04	-5.36561635400+02	1.6075213770+03
1.6664064500+00	1.28051165ED+04	-5.31266957100+02	1.60743497E00+03
1.6675170140+00	1.26527260110+04	-5.26045474100+02	1.60660665400+03
1.6668449820+00	1.24995591910+04	-5.20914032820+02	1.60602049500+03
1.6657834530+00	1.234675270D+04	-5.15527812900+02	1.60510001550+03
1.6709519390+00	1.21932536640+04	-5.10634461300+02	1.60400092430+03
1.6721325580+00	1.20393677790+04	-5.05935559260+02	1.60279112600+03
1.6733310590+00	1.18651222E0+04	-5.01127.5550+02	1.60131922300+03
1.6745443620+00	1.17305128300+04	-4.95406210650+02	1.59970650300+03
1.6757846950+00	1.15754928200+04	-4.9172401810+02	1.59757066300+03
1.6770433580+00	1.14201073800+04	-4.87125341300+02	1.59551607620+03
1.6783159770+00	1.12643543300+04	-4.8269-5H1200+02	1.59371341500+03
1.6777611343D+00	1.11068232010+04	-4.76170695000+02	1.591306550+03
1.6809274860+00	1.09517264660+04	-4.73797621 00+02	1.5-4663 665+03
1.6822646430+00	1.07944H13050+04	-4.6546432000+02	1.5-56373350+03

1.6505035829D+00	1.0477047222D+04	-4.4210524771D+02	1.574418...
1.6664069922D+00	1.0321754510D+04	-4.5546293110D+02	1.575687+6630+C1
1.6672327710D+00	1.0163331476D+04	-4.5275504920D+03	1.573061733D+C1
1.6892422140D+C0	1.0004443531D+04	-4.4465225450D+C3	1.5675+244.1D+C1
1.6907557150D+00	9.8451851590D+03	-4.4467951590D+02	1.563261956D+C1
1.6722538540D+0C	9.6854965250D+03	-4.4071209040D+02	1.555C113450+C1
1.6937772580D+00	9.5254006260D+03	-4.3676531519D+02	1.5541041120+C1
1.6953265650D+0C	9.3642552950D+03	-4.3249456560D+02	1.5450537170+C1
1.6969024520D+0G	9.2039734920D+03	-4.2646520630D+03	1.5434032540+C1
1.69850562310D+00	9.0426376160D+03	-4.2510957106D+C2	1.5775147223+C1
1.7300136442D+00	8.8804642150D+03	-4.2126049520D+02	1.5314856450+C1
1.7017968780D+00	8.7186603900D+03	-4.1742470370D+02	1.5250C20732D+C1
1.7034865570D+00	8.5560295140D+03	-4.1365526800D+C3	1.5112396540+C2
1.7052067470D+0G	8.3929655760D+C3	-4.0579495360D+C2	1.5111146430+C1
1.7069583610D+00	8.2294475430D+03	-4.0571411130+02	1.5036402150+C2
1.7087423670D+00	8.0654903780D+03	-4.0215510310D+02	1.4959806220+C2
1.7105597860D+00	7.9010959060D+03	-3.9533632350D+02	1.4476C2541D+C3
1.7124017020D+0C	7.7362270180D+03	-3.9449821850D+02	1.4790019453D+02
1.7142932550D+00	7.5709069640D+03	-3.9064411920D+02	1.4730047E4C+C2
1.7162236550D+00	7.4051302590D+03	-3.8677528830D+03	1.4656752C4C+C2
1.7181362199D+00	7.2388640390D+03	-3.8267686655D+02	1.4506691110C+C2
1.7201842530D+00	7.0721636390D+03	-3.7854947610D+02	1.4436634728+C2
1.7222312310D+00	6.9049715240D+03	-3.7455036790D+02	1.4360356767D+C2
1.7243168440D+00	6.7372971440D+03	-3.7058977600D+02	1.4165463525+02
1.7264466070D+00	6.5691338150D+C3	-3.6654195830D+02	1.4023892852+C2
1.7286223560D+00	6.4004831430D+03	-3.6284779650D+02	1.3953253311+C2
1.7309846C08D+00	6.2313319740D+03	-3.5869435710D+02	1.3618221532+C2
1.7331119622D+00	6.0616774040D+03	-3.5447860630D+02	1.3667765332+C3
1.7354454200D+00	5.8915167150D+03	-3.5019791050D+02	1.3562035833+C2
1.7378257960D+00	5.7208355310D+03	-3.4503605620D+C2	1.3420771570+C2
1.7402633410D+00	5.5496307780D+03	-3.4139483070D+02	1.3271377422D+C1
1.7427608730D+G0	5.3778955300D+03	-3.3646250020D+02	1.3120506070C+C2
1.7453214530D+0C	5.2056619125D+C3	-3.3223000830D+02	1.2961161171D+C2
1.7479434210D+00	5.0327964820D+03	-3.2749228A20D+02	1.2755905732C+C2
1.7506454350D+00	4.8594114350D+C3	-3.2263320420D+02	1.2602335110D+C2
1.7534165120D+00	4.6854601230D+03	-3.1764873460+02	1.2443722820+C2
1.7562660760D+00	4.5109250540D+03	-3.1252207990D+02	1.2256534750+C2
1.7591990280D+00	4.3357983280D+03	-3.0724464630D+02	1.2061415670+C2
1.7622208060D+00	4.1600621930D+C3	-3.0179919790D+00	1.1857392743C+C1
1.7653374850D+00	3.9837042890D+C3	-2.9617330250D+02	1.1645577770+C2
1.7685558740D+C0	3.8067045670D+03	-2.9034705330D+02	1.1472753610+02
1.7718836580D+00	3.6290472650D+03	-2.8430490090D+02	1.1151856620+C2
1.7753295530D+00	3.4507072550D+03	-2.7802154690D+02	1.0541266300+C1
1.7789035130D+00	3.2716644140D+03	-2.7147729290D+02 -	1.0655606650+C2
1.7826165960D+0C	3.0918886729D+03	-2.6464218870D+02	1.0428442510+C2
1.7864432890D+00	2.9113504580D+03	-2.5747714820D+02	1.0146299250+C2
1.7905179540D+00	2.7300159410D+C3	-2.4997714520D+02	9.8534523690+C1
1.7947304030D+00	2.5478406670D+03	-2.4206947480D+02	9.5424982350+C1
1.7951696940D+00	2.3647787610D+G3	-2.3371783970D+02	9.2127777839C+C1
1.8038356150D+00	2.1807730480D+03	-2.2466531390D+02	8.6653059530+C1
1.8007702390D+00	1.9957543460D+03	-2.1544293840D+02	8.4946672310+C1
1.8140151950D+00	1.8096375650D+03	-2.0536587750D+02	8.0948718235+C1
1.8156241220D+0C	1.6223173240D+03	-1.9452293560D+C2	7.6741274710+C1
1.8256681440D+00	1.4336563960D+C3	-1.8279520330D+02	7.2154505870+C1
1.8322450440D+00	1.2434711230D+03	-1.6998127470D+02	6.716277904C+C1
1.8394957490D+00	1.0515034050D+03	-1.5522953341D+02	6.1670196220+C1
1.8476367740D+00	8.5734645020D+02	-1.3995287370D+02	5.5524110550+C1
1.8570329900D+00	6.6042553617D+02	-1.2171732470D+02	4.4517451760+C1
1.8693566560D+00	4.5946763660D+02	-9.9910462830D+01	4.0164591550+C1
1.8735635910D+00	2.5143045460D+02	-7.1465946660D+01	2.5315504767D+01
1.9219421900D+00	5.0644262830D+00	-5.0644262830D+00	4.0544444300+C1
1.9629820240D+00	1.2623574670D+02	5.3724661260D+01	1.6520666FF10+C1
1.9808322210D+00	2.8482466110D+02	7.4732506610D+01	2.6731014110+C1
1.9348862670D+00	4.4942345210D+02	1.9245945950+01	3.2445905936D+C1
2.0069842260D+00	6.1697971190D+02	1.0433164500+02	1.655623455C+C1
2.01383346C0D+00	...	...	...

2.027814925D+00	9.567330876D+02	1.1475676570+02	4.36.601+391+01
2.037127144D+00	1.12752670ED+03	1.22-344-64ND+02	4.461764507C+01
2.0459224390+00	1.2946233150+03	1.2616567340+02	4.536096444C+01
2.0542926430+00	1.4716471910+03	1.3262451600+02	5.025201-390+01
2.0623109280+00	1.6438690630+03	1.3644234380+02	5.1647324540+01
2.0700303850+00	1.8161901-6C+03	1.3971754770+02	5.330694-400+01
2.0774544910+00	1.986532157D+03	1.4252602430+02	5.454300425D+01
2.0847345720+00	2.160834268D+03	1.4453632440+02	5.561190-650+01
2.091774067D+00	2.333045226C+03	1.46993530507U+02	5.6515P4.5CC+01
2.0986470870+00	2.5051210520+03	1.48742110860+02	5.733079576C+01
2.1053600950+00	2.67702655930+03	1.50217540800+02	5.9010243410+01
2.1119327090+00	2.8467357C20+03	1.51451419900+02	5.65569205C+01
2.1183782690+00	3.0202169280+03	1.52464782360+02	5.52630744 0+01
2.1247082880+00	3.1914457760+03	1.5329264670+02	5.944203115C+01
2.1309327740+00	3.3624145550+03	1.5354235910+02	5.957-1130330+01
2.1370605010+00	3.5330535800+03	1.5443700660+02	6.0026095560+01
2.1430992120+00	3.7034726390+03	1.5479015660+02	6.0205230730+01
2.1450557680+00	3.8735375160+03	1.55016125C0+02	6.0331670650+01
2.1549363600+00	4.0432760230+03	1.5512695030+02	6.0358365160+01
2.1607463240+00	4.2126774460+03	1.5513374620+02	6.0414272520+01
2.1664907790+00	4.3817321590+03	1.5504607250+02	6.0343233261+01
2.1721741560+00	4.5504313250+03	1.5487266ED+02	6.030846730C+01
2.1775005340+00	4.7187670520+03	1.5462206470+02	6.0154224520+01
2.1833736310+00	4.8867321350+03	1.5430085410+02	6.0042454660+01
2.1888964520+00	5.0543200670+03	1.539158F040+02	5.965615510C+01
2.1943733170+00	5.221524616D+03	1.5347305950+02	5.5637954500+01
2.1998055100+00	5.3683410230+03	1.5297778190+02	5.935003724C+01
2.2051972660+00	5.5547636510+03	1.5243536480+02	5.911456330C+01
2.2105495030+00	5.7207880510+03	1.51-494765D+02	5.8613509600+01
2.2158660510+00	5.8864102240+03	1.5122512030+03	5.846870704C+01
2.2211472540+00	6.051626158D+03	1.505656026D+02	5.614140571C+01
2.2263972980+00	6.216432377D+03	1.49047476160+02	5.777454620C+01
2.2316162370+00	6.3808255970+03	1.491550592D+02	5.736824560C+01
2.2369064050+00	6.5448027780+03	1.4841134940+02	5.654352930C+01
2.2419604320+00	6.7083611380+03	1.4764423560+02	5.656414005C+01
2.2471068550+00	6.8714980430+03	1.4685692810+02	5.612563532C+01
2.2522201070+00	7.034211068D+03	1.4605175850+02	5.563795600C+01
2.2573105640+00	7.196498122C+03	1.4523067700+02	5.5217396240+01
2.2623795070+00	7.3583570730+03	1.4439566370+02	5.4743326560+01
2.2674281470+00	7.5197859580+03	1.4354651490+02	5.42565297370+01
2.2724576460+00	7.6807830670+03	1.4269076430+02	5.376319401C+01
2.2774691010+00	7.8413466360+03	1.4165398700+02	5.325686215C+01
2.2824635590+00	8.0014752010+03	1.4094944010+02	5.274607667C+01
2.2474420070+00	8.1611672660+03	1.4006642050+02	5.227554459C+01
2.2924053940+00	8.3204215850+03	1.3918193500+02	5.165606943C+01
2.2973546170+00	8.4792367480+03	1.3825116C20+02	5.111642506EC+01
2.3022905490+00	8.6376116760+03	1.3735692600+02	5.062469705C+01
2.3072140160+00	8.7955452070+03	1.3650013170+02	5.006602656C+01
2.3121258100+00	8.9530362780+03	1.3560156650+02	4.953076232C+01
2.3170266940+00	9.11008415ED+03	1.3470167850+02	4.597751390C+01
2.3219173830+00	9.2666875210+03	1.33601468370+02	4.84207170330+01
2.3267986010+00	9.422845A630+03	1.3290119660+02	4.7865665950C+01
2.3316710100+00	9.5785582220+03	1.3200144000+02	4.7258422440C+01
2.3365352580+00	9.7338236760+03	1.31102-C520+02	4.6733606C7C+01
2.3413519890+00	9.8886415890+03	1.3020516BC0+02	4.61774246IC+01
2.3462417910+00	1.0043011920+04	1.2930946800+02	4.555466030C+01
2.3510852590+00	1.0196933120+04	1.28415614ED+02	4.502C95507C+01
2.3559225730+00	1.0350404560+04	1.275232657D+02	4.446149777C+01
2.3607554630+00	1.0503426650+04	1.26634665310+02	4.3951866280C+01
2.3655832740+00	1.0655997590+04	1.2574775700+02	4.332129244C+01
2.3704069100+00	1.080811311D+04	1.246636C9600+02	4.2752374740C+01
2.3752288790+00	1.0959576600+04	1.2356219740+02	4.2163015650C+01
2.3800436820+00	1.111100311C+04	1.2310343660D+02	4.161525114D+01
2.3848577770+00	1.126176F820+04	1.2222767660D+02	4.10462245C+01
2.3896696320+00	1.1412077740+04	1.213554457500+02	4.04245486C+01

2.3352?-3590D+00	1.1711335?6ED+C4	1.1?6165277D+02	3.?5?2?551?1?+??
2.40405619?5D+00	1.1?6025736CD+C4	1.1?75152550D+02	3.67?545106D+C?
2.4049034880D+00	1.2002761660D+04	1.17?6?56860D+02	3.?2?723?36C+C?
2.4137106930D+0G	1.2156620720+04	1.17?3??A77D+02	3.76-13??6?1D+C?
2.419519?1890D+0C	1.2304404260+04	1.1617100390D+02	3.712?C01730+01
2.4233264060D+00	1.2451531590D+C4	1.1531514740D+02	3.657735??2C+C?
2.42?1356990D+0G	1.25982C2?6ED+04	1.1446154540D+02	3.6C?55?62?+C?
2.4329464700D+00	1.2744417640C+C4	1.13?C?10610D+02	3.54?4?31?3C+C?
2.4377590600D+00	1.2?3?6174?1C+04	1.1275?66960D+02	3.454324?96C+C?
2.442573?660D+00	1.3035474720D+04	1.11?0?32?2?D+02	3.44?454767C+C?
2.4473912290D+00	1.31?0316560D+C4	1.1106120630D+02	3.?6?7CC-261C+G?
2.4522115150D+00	1.3324700470D+04	1.1021362700D+02	3.???7C?2?C+C?
2.4570350460D+0C	1.3468625?30D+C4	1.?5?6695?30D+02	?.2?11117130+C?
2.4618621070D+00	1.3612091400D+04	1.0?52044260D+02	3.22?7201670+C?
2.4666532740D+00	1.?755057970D+04	1.0767400260D+02	3.176?2434?D+C?
2.4715286280D+00	1.3857644620D+04	1.06?2743310D+02	3.12?12212-C?C?
2.4763635900D+0C	1.4039731190C+C4	1.0?6?020250D+02	3.07??526?C2C+01
2.4612134770D+00	1.4181357C00D+04	1.051322?220D+02	3.C2?14650?C+01
2.4860636150D+00	1.4322521820D+04	1.042?32?590D+02	2.9727?5?77C+C?
2.4909193240D+0C	1.4463225110D+C4	1.03432?3310D+02	2.52??64677C+C?
2.4957809170D+00	1.46?3466670D+04	1.C256C5?140D+02	2.6?3?77?46D+C?
2.5006486900D+00	1.4743245480D+04	1.017266?970D+02	2.?24?36429C+01
2.5055229850D+00	1.4862562C20D+04	1.UL?6999560D+02	2.77?74643?C+C?
2.5104049810D+00	1.5021414950D+04	1.00C010??220D+02	2.727614126C+C?
2.5152922950D+00	1.5159804320C+04	9.91???6330CD+01	2.6???44?710+C?
2.5201875310D+00	1.5297729570D+04	9.62?357?570D+01	2.6?2743?6?C+C?
2.5250912770D+00	1.5435189950D+04	?.74147906?0D+01	2.5??C160130+C?
2.5330026490D+00	1.5572165360D+04	9.6541917-10D+01	2.5??765642?+C?
2.5349223340D+00	1.5708715300D+04	9.56?4510450D+01	2.45?5?6??6?C+C?
2.5398506370D+00	1.584477?490D+04	9.47??1?1640D+01	2.44?713?3?2?D+C?
2.5447878250D+00	1.59?0375C30D+C4	9.3?67?32760D+01	2.40?51?47?0+C?
2.5457342340D+00	1.6115504550D+04	5.30C53273-0D+01	2.?5?6172730+C?
2.5546901240D+00	1.6250166160D+C4	9.210?1?7350D+01	2.31?6101250+C?
2.5596558010D+00	1.63?435?15C+04	9.120542?210D+01	2.37??C0??13D+C?
2.5646315690D+00	1.6?1808327D+04	9.C2?63??5700D+01	2.22??713?15?+0?
2.5656176950D+00	1.6651337630D+04	?.93?1071430D+01	2.1?73?4L?6C+C?
2.5746144860D+00	1.6784121850D+04	?.84?6?905570D+01	2.14???0??6CD+C?
2.5796222200D+00	1.6916435040D+04	?.752?85?660D+01	2.1042?2??54C+C?
2.5?46641201D+00	1.7048276610D+04	?.65?3547760D+01	2.0?3??22?CC+C?
2.5896717410D+00	1.7179646C70D+04	?.564?5153?0D+01	2.023?0??63?D+C?
2.5947140800D+00	1.7310542480D+04	?.469773C930D+01	1.9?3?3577?C+01
2.5997685430D+00	1.7440965180D+04	?.3737?5317D+01	1.9441719?3?+C?
2.6048354220D+00	1.7570913710D+04	6.2769345900D+01	1.90?541?3??0+C?
2.6099149860D+00	1.77003866?6D+C4	8.17?259?40D+0?	1.?671175437+G?
2.6150075570D+00	1.7829384090D+C4	?.C?06570?54D+01	1.?2?44?3?72?+C?
2.6201134500D+00	1.7957904620D+04	7.5?11?51260D+01	1.7?3221541?+C?
2.6252329070D+00	1.8085947810D+04	7.6?0717106?D+01	1.7555111?4?C+C?
2.6303662700D+00	1.?213?12360D+C4	7.77?3021320D+01	1.71??1C3??0?+C?
2.6355138050D+00	1.8340597760D+04	7.676921296?D+01	1.6?3615250?C+G?
2.6406758310D+00	1.8467203070D+04	7.5735351770D+01	1.6?4?4370110+0?
2.6458525661D+00	1.8593327640D+04	7.46?0998250D+01	1.6137?26?71C+01
2.6510445600D+00	1.8718965560D+04	7.36?653718D+01	1.57?5?5?4?46C+C?
2.6562518970D+00	1.8844129690D+04	7.2571247570D+01	1.5455?3?614C+C?
2.6614749170D+00	1.8966805530D+04	7.14?5246540D+01	1.512776?C7C+C?
2.6667135540D+00	1.905299E520D+04	7.04?6342330D+01	1.4?6123??1C+C?
2.6719693360D+00	1.5216701880D+04	?.93101?50700D+01	1.447570155?C+C?
2.6772413610D+00	1.5339920170D+04	6.8?201043940D+01	1.416?172?2?C+G?
2.6?25303590D+00	1.946265?820D+04	?.7C?0297120D+01	1.3??162167C+G?
2.6978366620D+00	1.95?4892290D+04	?.5?46303316D+01	1.?54?C3?41C+G?
2.6931160491D+00	1.5706643760D+04	?.4?C4602160D+01	1.324237?6?6C+G?
2.6985023080D+00	1.9?27904C30D+04	?.3649?5?906D+01	1.2?46E3?7E2?C+C?
2.7039623570D+00	1.55?8671780D+04	6.24?250172D+01	1.2?4?7?24?CC+C?
2.7092410150D+00	2.0066996120D+04	6.1?C3721170D+01	1.23?7?1?5?C+C?
2.71463?6050D+00	2.01?8725590D+04	?.011323306ED+01	1.2C?5677?1C+C?
2.7200554560D+00	2.0?36009160D+04	5.??10?51620D+01	1.1??F3?6?2C+G?

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2.730948309D+00	2.054506263D+04	5.647072465D+01	1.124 051221+0
2.736425015D+00	2.066267050D+04	5.523253075D+01	1.10 50074650+0
2.741522362D+00	2.07 015650D+04	5.39433167+D+01	1.274663260+0
2.747440738D+00	2.069694063D+04	5.272205292D+01	1.2472545360+0
2.752980474D+00	2.101322031D+04	5.144926436D+01	1.0243742 1C+0
2.758541569D+00	2.112894600D+04	5.016473552D+01	0.9555905556+0
2.764125562D+00	2.1244261400D+04	4.986647662D+01	4.7556257240+0
2.769731641D+00	2.135902053D+04	4.756172071D+01	4.5242634540C+0
2.775360601D+00	2.147326535D+04	4.624326231+0+01	5.2534341260+0
2.781012009D+00	2.154700656D+04	4.45131162+D+01	5.0670444200+0
2.786684655D+00	2.170023055D+04	4.357374614D+01	4.445075 23+0
2.792388552D+00	2.181253956D+04	4.222262563)+01	4.6274655640+0
2.798112867D+00	2.192513265D+04	4.061762320+01	5.414245652C+0
2.803862C68D+00	2.203680751D+04	3.945024110+01	4.2053043420+0
2.809636512D+00	2.214756253D+04	3.815902C65D+01	4.0036252600+0
2.815436645D+00	2.225859565D+04	3.671609253D+01	7.6001664450+0
2.821262880D+00	2.236870556D+04	3.531767657D+01	7.603665122C+0
2.827115671D+00	2.247629026D+04	3.390865360+01	7.411735655C+0
2.832995431D+00	2.258734754D+04	3.249050103D+01	7.2236655720+0
2.838902628D+00	2.269587666D+04	3.106464651D+01	7.0356764510+0
2.844837706D+00	2.280387455D+04	2.953060762D+01	6.855673217C+0
2.850801125D+00	2.291133763D+04	2.816507676D+01	6.6636344560+0
2.856793345D+00	2.301826591D+04	2.674045076D+01	6.511461420+0
2.862814852D+00	2.312466334D+04	2.526533666D+01	6.342321124C+0
2.868866150D+00	2.323051795D+04	2.362400712D+01	6.175751731D+0
2.874947712D+00	2.333583158D+04	2.235707C20D+01	6.01-CEC2150+0
2.881060036D+00	2.344060211D+04	2.086503+30+01	5.861CH47870+0
2.887203643D+00	2.354482735D+04	1.940844233D+01	5.7077465470+0
2.893379056D+00	2.364850526D+04	1.792762161D+01	5.5551053560+0
2.899586785D+00	2.375163343D+04	1.644362109D+01	5.4115551530+0
2.905827379D+00	2.385420567D+04	1.495702603D+01	5.2654051170+0
2.912101396D+00	2.395623170D+04	1.346803701D+01	5.1302635610+0
2.918409376D+00	2.405769713D+04	1.197757660D+01	4.594560740+0
2.924751904D+00	2.415860366D+04	1.046626160+01	4.662243155+0
2.931124550D+00	2.425894883D+04	8.994636234D+00	4.733215295+0
2.937542935D+00	2.435873025D+04	7.503985413D+00	4.607455513D+0
2.943992613D+00	2.445794536D+04	6.014527631D+00	4.484500665C+0
2.950479254D+00	2.455659184D+04	4.527106347D+00	4.365455620+0
2.957003454D+00	2.465466697D+04	3.042626064D+00	4.249195452D+0
2.963565850D+00	2.475216426D+04	1.561691376D+00	4.135546427D+0
2.970167122D+00	2.484909360D+04	8.557897511D-02	4.025665757C+0
2.976807902D+00	2.494543873D+04	-1.395200756D+00	3.916363706C+0
2.983488908D+00	2.504120267D+04	-2.845762066D+00	3.6135245120+0
2.990210843D+00	2.513638218D+04	-4.307244041D+00	3.712314455D+0
2.996974377D+00	2.523097444D+04	-5.756593210D+00	3.613476035C+0
3.003780257D+00	2.532497670D+04	-7.196919222D+00	3.517360355C+0
3.010622266D+00	2.541838626D+04	-8.627361104D+00	3.423504765D+0
3.017522082D+00	2.551120016D+04	-1.004680928D+01	3.333057514D+0
3.024459558D+00	2.560341574D+04	-1.145449356D+01	3.244763071D+0
3.031442444D+00	2.569502582D+04	-1.224910559D+01	3.156565367C+0
3.038471594D+00	2.579603968D+04	-1.423001931D+01	3.075609525C+0
3.045547781D+00	2.587644255D+04	-1.559577157D+01	2.994353523C+0
3.052671927D+00	2.596623527D+04	-1.694571651D+01	2.915555534C+0
3.059844841D+00	2.605541477D+04	-1.827652-490D+01	2.834636652C+0
3.067067447D+00	2.614357326D+04	-1.959334961D+01	2.765493566+0
3.074340708D+00	2.623192243D+04	-2.098830070D+01	2.653516233C+0
3.081665495D+00	2.631924456D+04	-2.216421352D+01	2.623650676D+0
3.089042746D+00	2.640559129D+04	-2.341411501D+01	2.555641615C+0
3.096473521D+00	2.649200371D+04	-2.464962561D+01	2.453034 0EL+0
3.103958796D+00	2.657744661D+04	-2.585753623D+01	2.426177552C+0
3.111499592D+00	2.666224403D+04	-2.704070022D+01	2.36421447 C+0
3.119096993D+00	2.674641351D+04	-2.415826453D+01	2.3640544550+0
3.126752065D+00	2.682993714D+04	-2.93287677D+01	2.245163556C+0
3.134465979D+00	2.691281678D+04	-3.043133216D+01	2.165170104C+0
3.142239804D+00	2.695504955D+04	-3.156473602D+01	2.134262653C+0

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3.1519721240D+00	2.7127559200D+04	-5.3459772310+01	2.022 2.1-210+0
3.1659330670D+00	2.7237432790D+04	-5.4539176150+01	1.5771454530+0
3.1739566930D+00	2.7317442200D+04	-5.5475055530+01	1.653474 500+0
3.1820508350D+00	2.7356390560D+04	-5.6396965520D+01	1.8832402700+0
3.1902104660D+C0	2.7474672490D+04	-5.7272086100U+31	1.653703470C+0
3.1984389760D+00	2.7552264030D+04	-5.8111095260-01	1.793857465C+0
3.2067379330D+00	2.7629224360D+04	-5.8651235680D+01	1.745675510+00
3.2151036020D+00	2.7705460400D+04	-5.9675013370+C0	1.70771113570+00
3.2235527140D+00	2.7791072530D+04	-6.0397451020D+01	1.666651663P+0
3.2320717710D+00	2.7855974840D+04	-6.1000207760D+01	1.627351540C+0
3.2406673590D+00	2.7930191700D+04	-6.1720665820D+01	1.549867530C+0
3.2493412260D+00	2.8003720160D+04	-6.2319222870D+01	1.551457333C+0
3.2580949940D+00	2.8076556570D+04	-6.2674130540D+01	1.515C605140+0
3.2669304720D+00	2.8148695180D+04	-6.3350667C00+01	1.471665507C+0
3.2758494880D+00	2.8220143660D+04	-6.3651000550+01	1.4452625 10+0
3.2848539410D+00	2.8250667510D+04	-6.4271356750D+01	1.411745066C+0
3.2939457750D+00	2.8360527650D+04	-6.4645336870D+01	1.37910435940+00
3.3031269650D+00	2.8430861210D+04	-6.4972353900D+01	1.3473043210+0
3.3123996530D+00	2.8458885270D+04	-6.5251613450D+01	1.3163C9460C+0
3.3217659190D+00	2.8566739640D+04	-6.5473117850+01	1.296065713C+00
3.3312240030D+00	2.8633993450D+04	-6.5665854960D+01	1.296556645C+00
3.3407880630D+00	2.8700472030D+04	-6.5735571150+01	1.227515126C+0
3.3504491130D+00	2.8766229570D+04	-6.5843626330+01	1.15971317300+0
3.3602125010D+00	2.8831264580D+04	-6.5918593420+01	1.17325195930+0
3.3700822680D+00	2.8895573330D+04	-6.5903411630+01	1.145406525C+0
3.3800598080D+00	2.8959153590D+04	-6.5838156650+01	1.115145441C+0
3.3901483660D+00	2.9022003020D+04	-6.5722878530+01	1.033453500C+0
3.4003506570D+00	2.9084119050D+04	-6.5557428630+01	1.056254050C+0
3.4106607700D+00	2.9145499490D+04	-6.5342040970+01	1.043647923C+0
3.4211086880D+00	2.9206141510D+04	-6.5076732410+01	1.0154501380+0
3.4316707270D+00	2.9266044330D+04	-6.4761957890+01	9.957597756C-01
3.4423590070D+00	2.9325204470D+04	-6.4379052400+01	9.725553924C-01
3.4531772480D+00	2.9383620460D+04	-6.3585182660+01	9.4973600450C-01
3.4641288470D+00	2.9441290130D+04	-6.3524119760+01	9.273292 440C-01
3.4752176950D+00	2.9498211860D+04	-6.3015569590+01	9.057116774C-01
3.4864475160D+00	2.9555438370D+04	-6.2460176850+01	8.8366545050C-01
3.4978224980D+00	2.9609806190D+04	-6.1858605340+01	8.623874154C-01
3.5093468940D+00	2.9664471540D+04	-6.1212391060+01	9.414517570C-01
3.5210251840D+00	2.9718364360D+04	-6.0522003870+01	8.20545E 6C0-01
3.5328618640D+00	2.9771541200D+04	-5.9786840230+01	8.005658479C-01
3.5448615180D+00	2.9823940460D+04	-5.9014177550+01	7.80C014310C-01
3.5570302640D+00	2.9875562050D+04	-5.8159587730+01	7.6052537160C-01
3.5693722950D+00	2.9926463720D+04	-5.7345895550+01	7.415625936D-01
3.5818936300D+00	2.9976568490D+04	-5.6455452430+01	7.224766564C-01
3.5945999040D+00	3.0025944630D+04	-5.5529686850+01	7.036703395C-01
3.6074573990D+00	3.0074542180D+04	-5.4570491340+01	6.851341797C-01
3.6205924900D+00	3.0122376620D+04	-5.3579783700+01	6.666755502C-01
3.6338918200D+00	3.0169447960D+04	-5.2559637170+01	6.466797544PC-01
3.6474025570D+00	3.0215755100D+04	-5.1512205040+01	6.311445498C-01
3.6611322430D+00	3.0261297840D+04	-5.0439798840+01	6.1367043680C-01
3.6750885260D+00	3.0306075830D+04	-4.9344719810+01	5.964542C300C-01
3.6892798660D+00	3.0350066890D+04	-4.8229515410+01	5.7945644520C-01
3.7037145420D+00	3.0393338440D+04	-4.7096728300+01	5.627543911C-01
3.7184030260D+00	3.0435815640D+04	-4.5549025630+01	5.462942597C-01
3.7333535810D+00	3.0477537290D+04	-4.4749179370+01	5.301576746C-01
3.7485779060D+00	3.0518485860D+04	-4.3619994700+01	5.142253690C-01
3.7640861460D+00	3.0558677520D+04	-4.2444346310+01	4.965435527C-01
3.7758900520D+00	3.0558100430D+04	-4.1265326430+01	4.831156136C-01
3.7960021630D+00	3.0636758270D+04	-4.0085275590+01	4.679510754C-01
3.8124356220D+00	3.0674653100D+04	-1.8596086070+01	4.530267066C-01
3.8292045290D+00	3.0711763460D+04	-1.7730110390+01	4.343754435C-01
3.8463237260D+00	3.0746150240D+04	-1.6576077670+01	4.235656000C-01
3.8638094950D+00	3.0793753800D+04	-1.5426172640+01	4.050044606C-01
3.8816785700D+00	3.0818544460D+04	-1.4291573730+01	3.955847505C-01
3.8999497450D+00	3.0852672530D+04	-1.3175454010+01	3.6221407300C-01

3.93777831?0+00	3.0491854159?+04	-1.10111656?+04	3.5???85???61-0?
3.9573775350+00	3.0950333670+04	-9.46719212400+00	3.42576-1?C?-0?
3.9774712570+00	3.0981363550+04	-8.95799578960+00	3.2?40123570-01
3.99804040000+00	3.1011631530+04	-7.96?4614660+00	3.1722?511??-0?
4.0192346000+00	3.1041137500+04	-7.0395?44390+00	3.04?475636?-01
4.0409670000+00	3.1069981130+04	-6.13743?44200+00	2.52?46??63?-01
4.0633116400+00	3.1057662010+04	-5.27711?C640+00	2.?661266?1?-01
4.086303982?+00	3.1125075980+04	-4.46?7576?30+00	2.6?732?711C-01
4.1059866870+00	3.1151552720+04	-3.69052100010+00	2.56?92730?0-01
4.1344048870+00	3.1177220660+04	-2.?6?3224600+0?	2.45?7?132??-01
4.1556071700+00	3.1202141970+04	-2.295?549370+00	2.33?7?5474?-01
4.1856487880+00	3.1226295090+04	-1.6745615460+00	2.2247?2463?-0?
4.2125895950+00	3.1249674110+04	-1.1055652456+00	2.1116701300-01
4.2404790900+00	3.1272288620+04	-5.59710?0C00-01	1.95?34652?0-01
4.2694483500+00	3.1294124660+04	-1.2744443100-01	1.4?773?732?-01
4.2955256530+00	3.1315162710+04	2.8C?5421660-01	1.7767?724?0-01
4.3308250630+00	3.1335455660+04	6.35 5352900-01	1.66650655??-01
4.3634545510+00	3.1354951790+04	5.37?356626?-01	1.556??5?7?0-01
4.3975366880+00	3.1373654530+04	1.16795591?0+00	1.44?0151930-01
4.4332130220+00	3.1391564520+04	1.3?7675?610+00	1.3?55976??7?-0?
4.4706439700+00	3.1408675460+04	1.5386302920+00	1.233014453C-0?
4.5100136620+00	3.1424982320+04	1.6440745340+00	1.1272913?55?-01
4.5515603440+00	3.1440479060+04	1.7059464540+00	1.02?1226?5??-01
4.5955253280+00	3.1455159250+04	1.727?2071?0+00	9.20?65??73?-0?
4.6422256440+00	3.1469015590+04	1.71341?2920+0C	8.20?556?00?-0?
4.6920361610+00	3.14?2041950+04	1.6668935840+00	7.23?7121770-0?
4.7454137810+00	3.1494229360+04	1.5928100010+00	6.3017203??5?-0?
4.8029240900+00	3.1505570180+04	1.4959?92970+00	5.40473??7?1?-0?
4.8652804090+00	3.1516055770+04	1.381?515190+00	4.55440?75?7?-0?
4.8918937330+00	3.1520197680+04	1.3321976500+00	4.227517155?-0?
4.9185070680+00	3.152370?650+04	1.2?2?71062?+00	3.92?6761530-0?
4.9451203970+00	3.152713?100+04	1.2342107160+0C	3.63?5636?4?-0?
4.9717337260+00	3.1530327730+04	1.1?654?7740+00	3.?6473795??-0?
4.9983470550+00	3.1533293110+04	1.14015630?0+00	3.11?44??52?-0?
5.0249603850+00	3.1536040790+04	1.095241059?+00	2.876?31?13?-0?
5.0515737140+00	3.153853934?0+04	1.05196529C0+00	2.66?0022??1?-0?
5.078187043?0+00	3.1540560690+04	1.01044725?0+00	2.45?171?54?-0?
5.1048003720+00	3.1542154610+04	9.70768112?0-01	2.26?45214?0-0?
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ECOMMENCED INTEGRATION LIMITS RMIN = -(1) = 1.400 FMAX =R(651)= 5.365

SUMMARY OF ERRORS OF THE INVERTED PERTURBATION APPROACH

J(J+1)	1.	2.	3.	4.	5.	6.	7.	8.	12ΩYFFA?Cζ
2.0	15.03964	3.85281	.791?4	.05260					

AVERAGE 16.24466   4.16151   .65529   .05461   2.2C000C00C-07

THE DUNHAM COEFFICIENTS

-4.98726373D-01   3.07267750D-01   2.2C000C00C-07
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-3.57101904D+00 -1.5C0C0C00D-05
2.65076374D-03
-1.29000000D-04

Appendix C

Supplementary References

The following are references which contain information about the reduction of spectroscopic data and the construction of potential energy curves. They were not cited elsewhere in this report.

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Vita

Lyle L. Rutger was born 13 July 1949. He graduated from Cisne Community High School, Cisne, Illinois in 1967. He graduated from Olney Community College in 1969 and then attended Southern Illinois University. In 1971 he entered the United States Air Force and served three years as a flight simulator technician. He was selected for the Airman Educating and Commissioning Program in 1975. Under this program, he received a Bachelor of Science degree in Mechanical Engineering from The Ohio State University and a commission in the United States Air Force in 1977. He served as a Reentry Vehicle Test Engineer, Project Manager and then Section Chief at the Air Force Rocket Propulsion Laboratory, Edwards AFB, California. He entered the School of Engineering, Air Force Institute of Technology in August 1981.

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4. TITLE *(and Subtitle)* NUMERICAL METHODS FOR THE PREPARATION OF POTENTIAL ENERGY CURVES OF DIATOMIC MOLECULES (with applications for lead-oxide)		5. TYPE OF REPORT & PERIOD COVERED MS Thesis
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) LYLE L. RUTGER Capt USAF		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Air Force Institute of Technology (AFIT-EN) Wright-Patterson AFB, Ohio 45433		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
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16. DISTRIBUTION STATEMENT *(of this Report)*

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Air Force Institute of Technology (ATC)
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7 APR 1983

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

Potential Energy Curve
Diatomic Molecule
Rydberg-Klein-Rees Method (RKR)

Inverted Perturbation Approach (IPA)
Lead-Oxide
Spectroscopy

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

This thesis presents the tools necessary to transform spectral data from diatomic molecules into potential energy curves which are most consistent with the experimental data and the quantum mech-anical model (i.e., the Schroedinger wave equation (SWE)) for a diatomic molecule. The first of these tools, a computer program called DUNCON, generates spectroscopic constants by performing least-squares fits to spectroscopic data. The program performs fits to

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separate groups of data and then merges the results in a manner based upon the relative errors and correlations of the separate data sets. The second tool is a computer program provided by C. R. Vidal which contains two major routines. The first routine generates potential energy curves using the Rydberg-Klein-Rees (RKR) method. The second routine through an inverted perturbation analysis (IPA) adjusts the RKR curve so it is consistent with the SWE model. Finally, techniques are presented for extending potential energy curves to the dissociation energy, De , when the spectroscopic data alone is inadequate for the purpose.

Use of the programs is demonstrated for the diatomic molecule lead-oxide. Constants are produced for the A, B, D, a, b, and X states from previously published experimental data. A new set of assignments is made for the b state experimental data producing constants with significantly improved accuracy over those reported in literature. The b state constants are:

$$T_e = 16325.1 \pm 11.2 \text{ cm}^{-1}$$

$$W_e = 430.99 \pm 2.47 \text{ cm}^{-1}$$

$$W_e X_e = -0.757 \pm 0.441 \text{ cm}^{-1}$$

These are one standard error limits. Potential energy curves are generated for the a, A, and X states of lead-oxide. The X state potential energy curve is extended to its dissociation energy.

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